Oriented crystallization of ultra-thin (2 nm) gold nanoplatelets inside a reactive hydrophobic polymeric matrix

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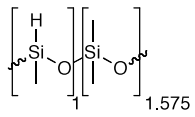
Supporting Information

1) Experimental

Calculations for the molecular weight of the repeating unit of polymer **2**:

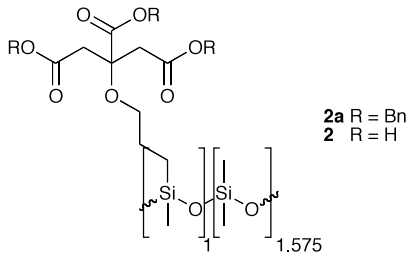
^{1}H NMR of the starting methylhydrosiloxane-dimethylsiloxane copolymer (molecular weight: 900-1200; 50-55% molar Si-H; Gelest) shows a relative integration of 1 for the proton at 4.1 ppm (OSiMe*H*) versus 12.45 for the methyl protons (OSi(C*H*3)$_2$ and OSi(C*H*$_3$)H), which yields the formula:



which correlates, considering the molecular weight of each fragment, to a total molecular weight of 176.55 for the repeating unit.

After hydrosilylation with tribenzyl allyloxycitrate (MW of 502.57), the molecular weight of the repeating unit becomes 679.12.

Following deprotection of the benzylic esters, the calculated molecular weight for a repeat unit is 409.12.



At a concentration of 3mg.mL-1, the concentration of repeating unit (and thus of citrate head group) is 7.33 mM.

Knowing that the gold salt concentration is 5mM, the ratio of citrate/Au^{3+} is 1.466 in the process yielding the hyperbranched gold nanocrystals.

2) Additional Images

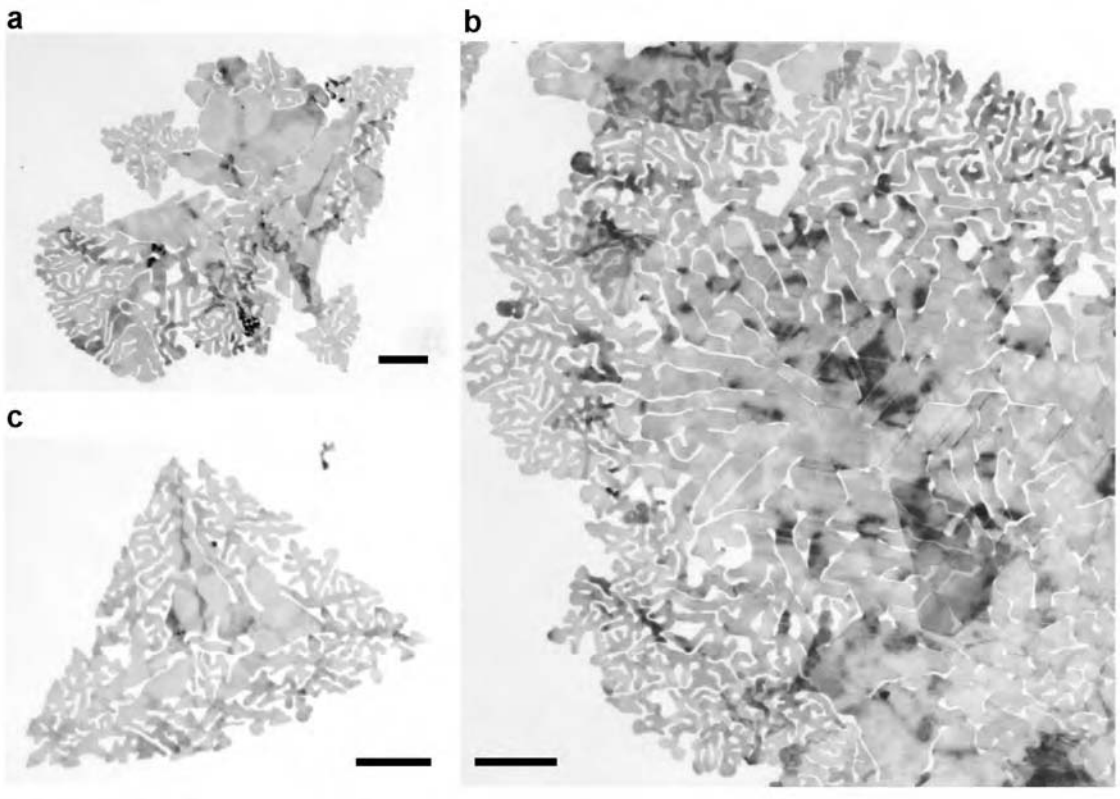


Figure S1. Representative TEM images of gold dendritic nanoplatelets prepared by simply mixing a gold salt and polymer **2**. Typical morphologies include large, extended nanoplatelets with a more dendritic or hyperbranched features at the periphery (a,b and c). All scale bars represent 100nm.

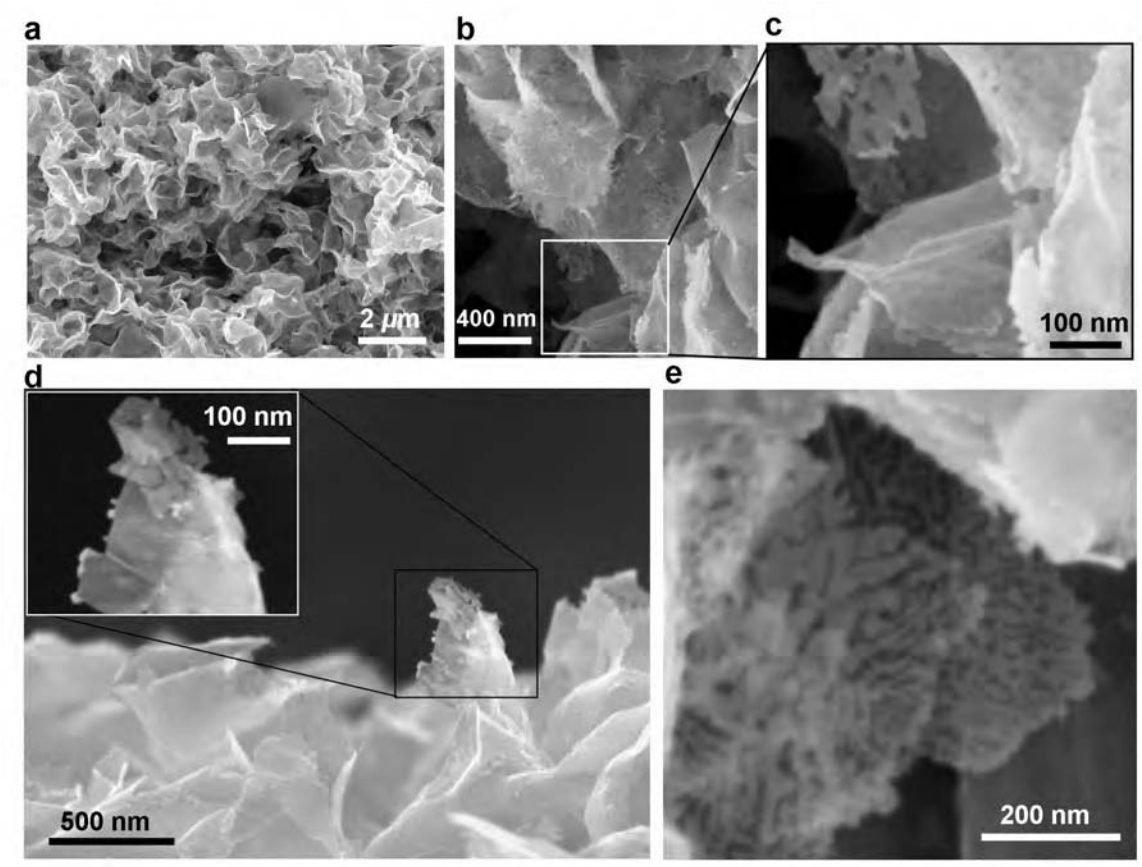


Figure S2. (a, b) Representative SEM images of gold nanoplatelets prepared by simply mixing a gold salt and polymer **2**. At low magnification, the nanoplatelets appear as a folded tissue (a). At mid magnifications (b, c), the platelet morphology becomes more evident. The low contrast allows the view stacked multiple nanoplatelets. At high magnification (d, e), the extremely low thickness of the nanoplatelets is now evident, as well as their dendritic nature (e).

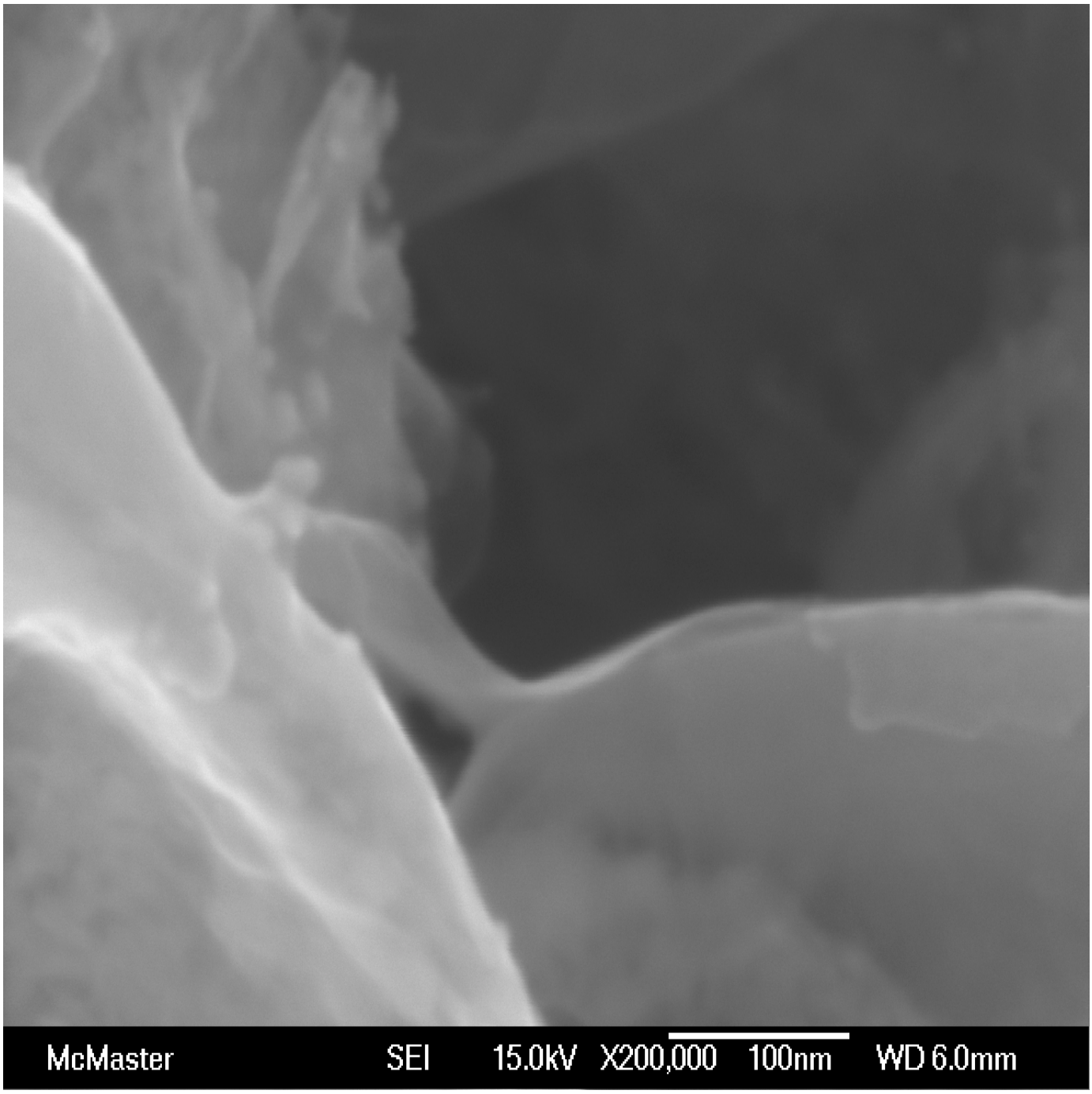


Figure S2-2. Full-scale SEM image of gold nanoplatelets prepared by simply mixing a gold salt and polymer 2. High magnification reveals the extrememely low thickness of the gold nanocrytals.

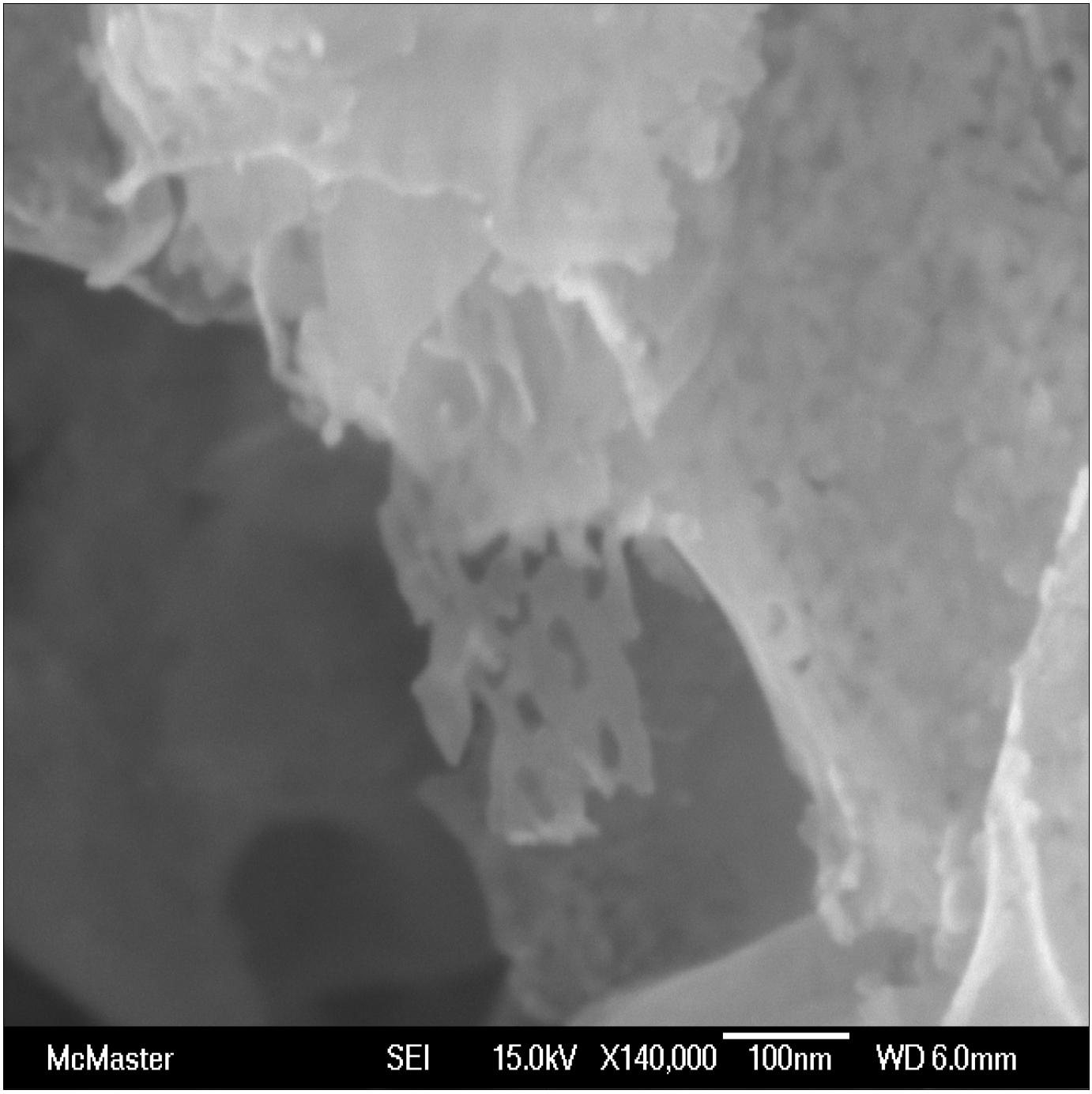


Figure S2-3. Full-scale SEM image of gold nanoplatelets prepared by simply mixing a gold salt and polymer 2. High magnification reveals the extrememely low thickness of the gold nanocrytals.

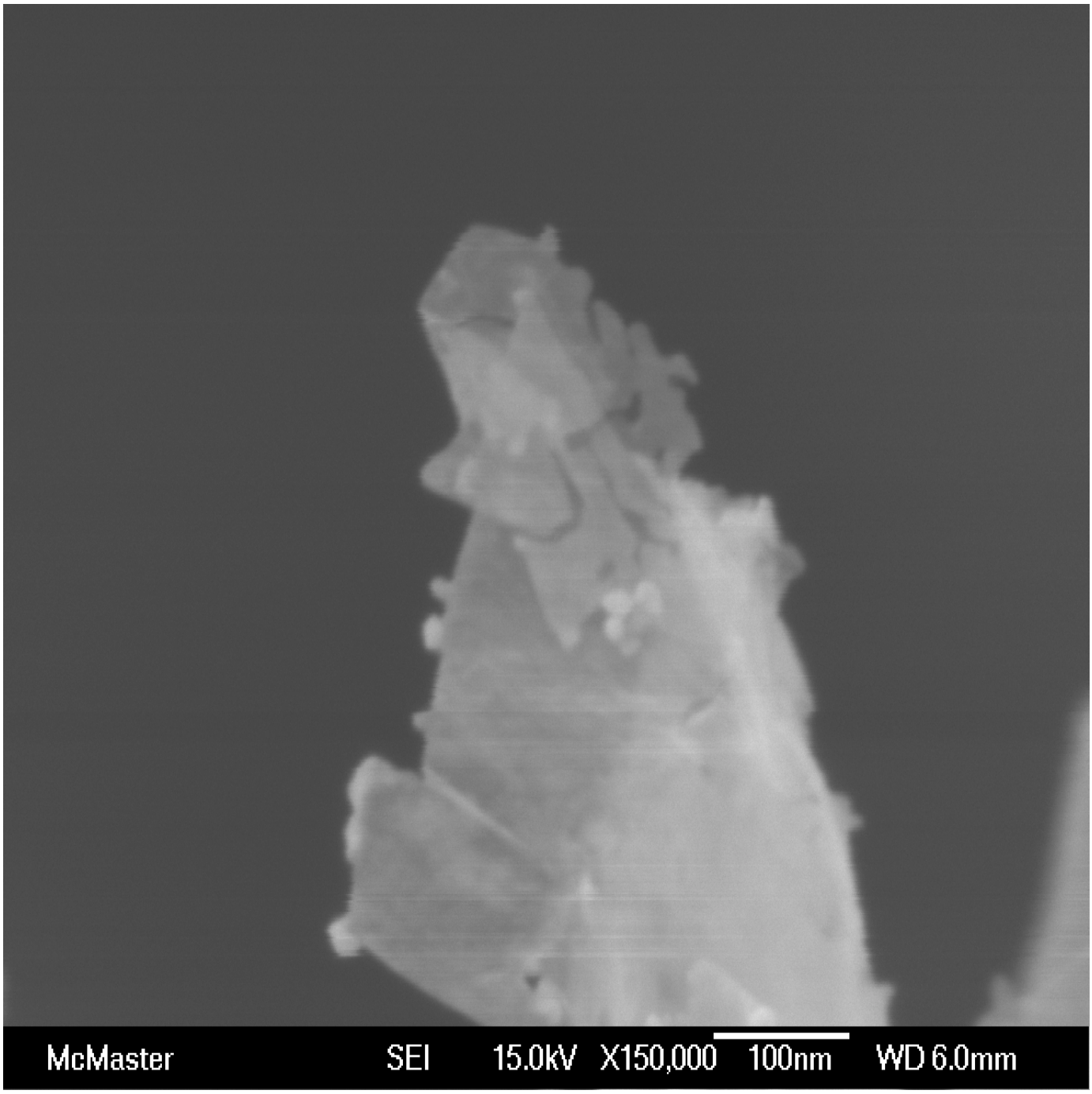


Figure S2-4. Full-scale SEM image of gold nanoplatelets prepared by simply mixing a gold salt and polymer 2. High magnification reveals the extrememely low thickness of the gold nanocrytals.

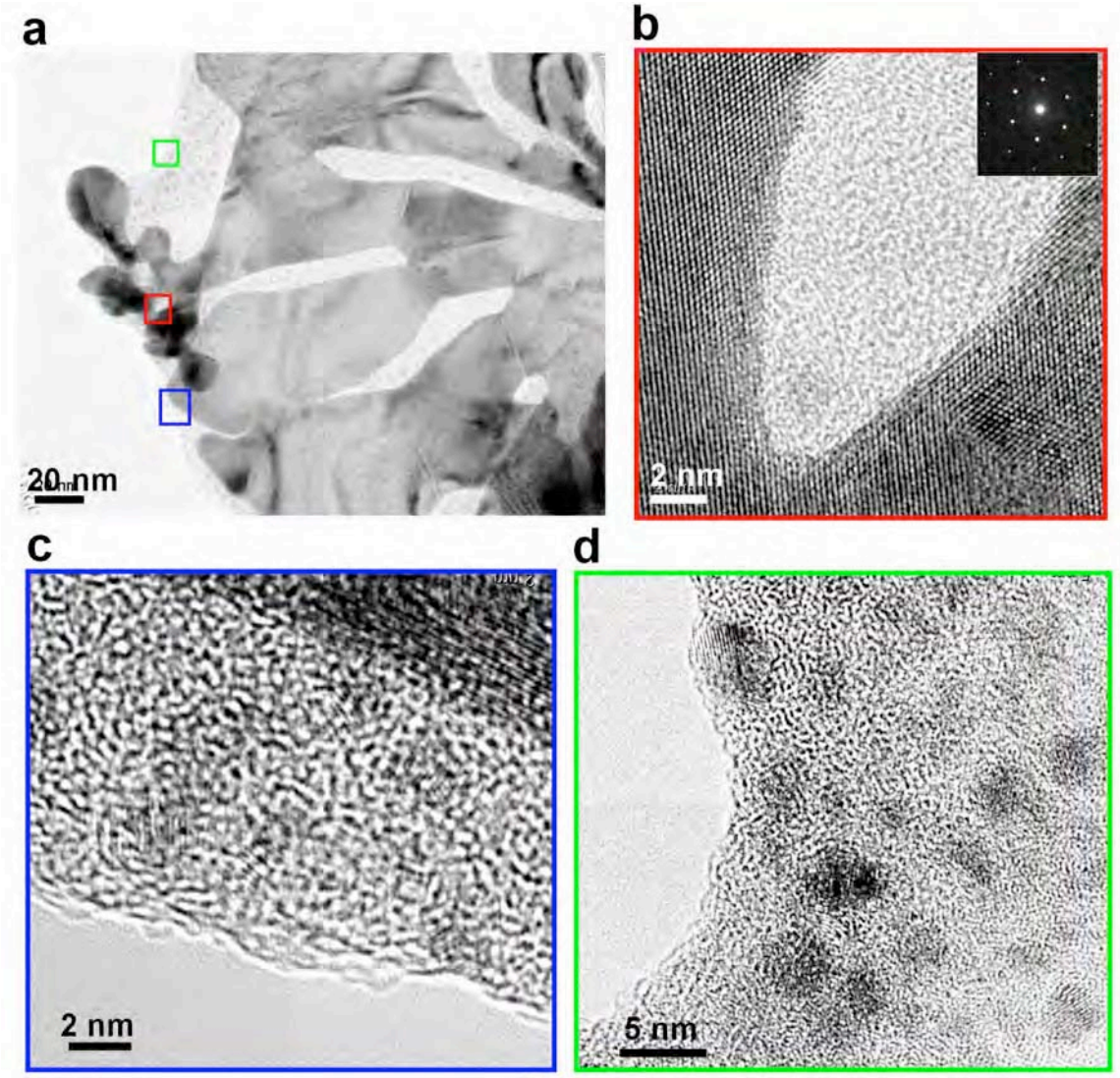


Figure S3. Representative High-ResolutionTEM images of gold nanoplatelets prepared by simply mixing a gold salt and polymer **2**. (a) shows the periphery of a dendritic gold nanoplatelet. The presence of polymer **2** is evident from the image, as well as the presence of small gold crystallites embedded in the polymeric matrix. The colored squares represents the areas showed in b,c and d. (b) shows continuous lattice fringes, indicating the crystalline nature of the nanoplatelets. (c) shows the presence of a polymeric layer of **2** at the surface of the nanoplatelets. Small gold crystallites are embedded in the polymeric matrix, as shown in (d),

3) pH-dependance: UV-Kinetic study

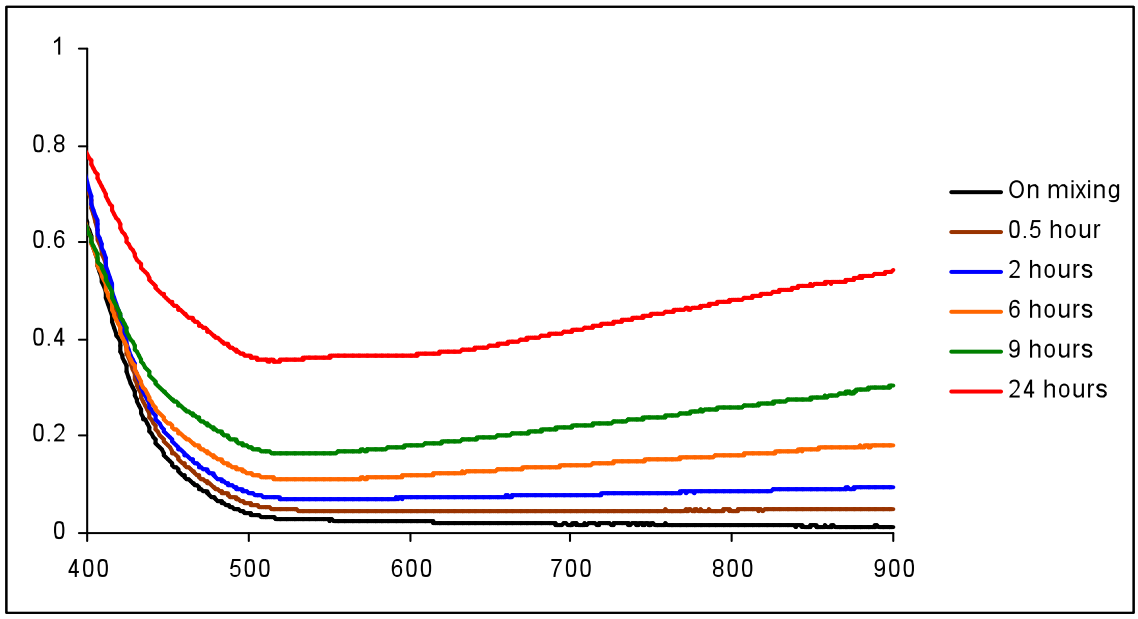


Figure S4 UV-Visible kinetic of gold reduction with polymer **2** at pH = 4 (with a ratio citrate to gold equal to 1.5). The spectra are directly comparable and demonstrate the speed of reduction and the type (nanoplatelets) of gold products obtained. No nanoparticles are produced at this pH.

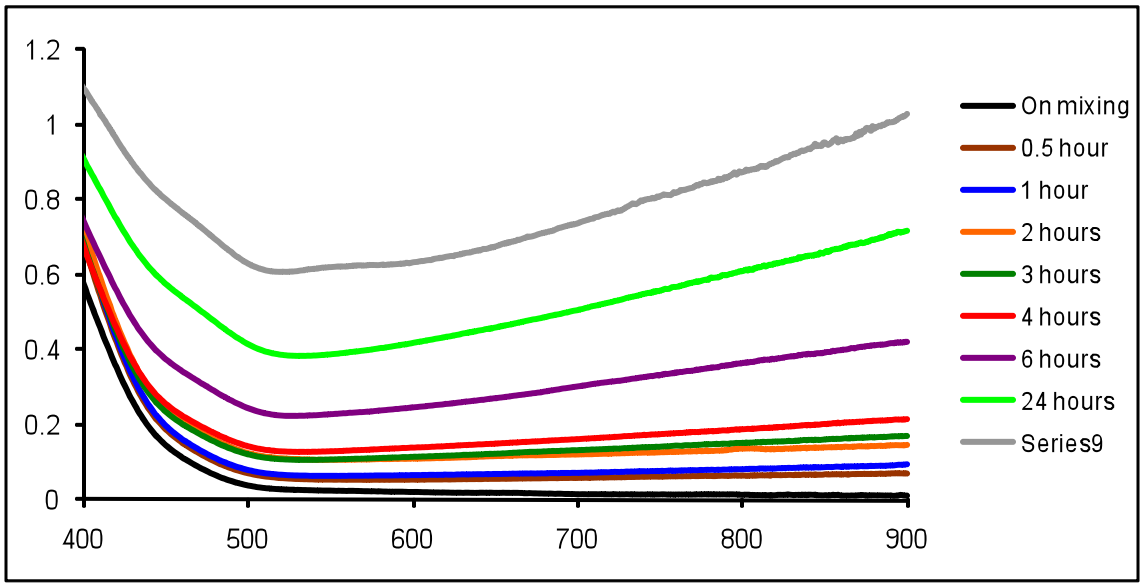


Figure S5 UV-Visible kinetic of gold reduction with polymer **2** at pH = 5 (with a ratio citrate to gold equal to 1.5). All spectras are directly comparable and demonstrate the speed of reduction and the type (nanoplatelets) of gold products obtained. No nanoparticles are produced at this pH.

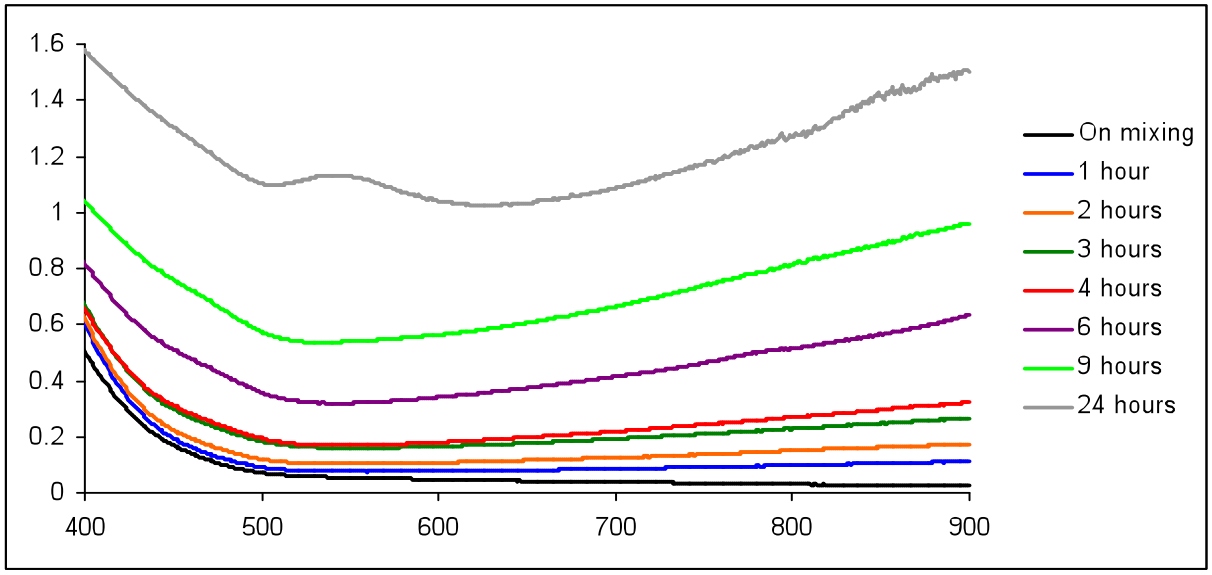


Figure S6 UV-Visible kinetic of gold reduction with polymer **2** at pH = 6 (with a ratio citrate to gold equal to 1.5). All spectras are measured at the same scale and demonstrate the speed of reduction and the type (nanoplatelets) of gold products obtained. A marginal number of nanoparticles were produced, at the very end of the reduction process.

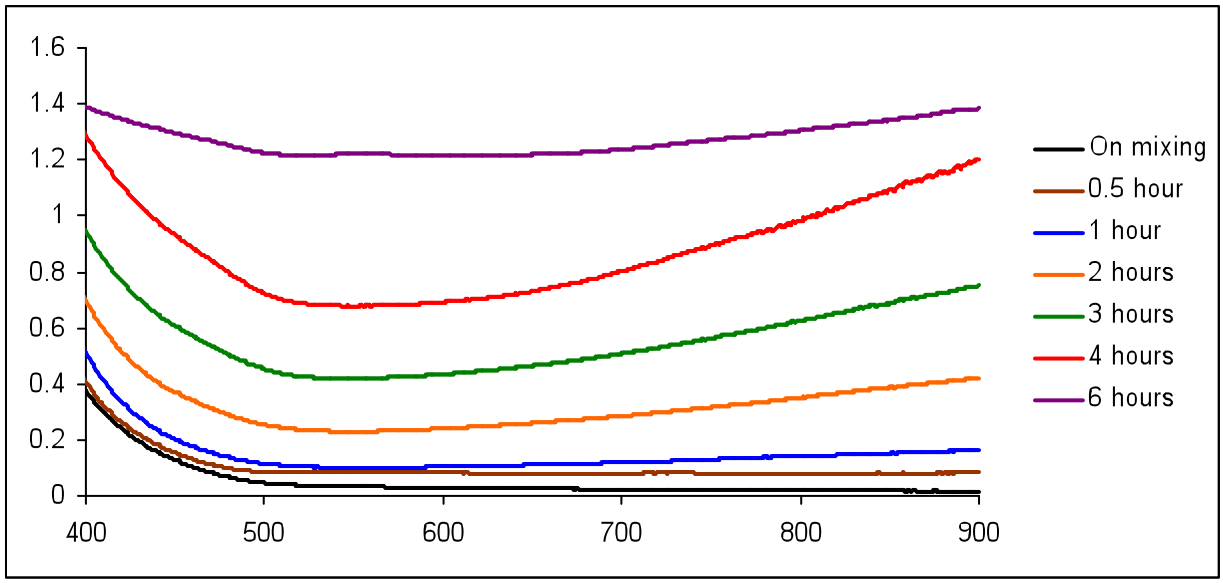


Figure S7 UV-Visible kinetic of gold reduction with polymer **2** at pH = 7 (with a ratio citrate to gold equal to 1.5). The 6 first spectra are direclty comparable and demonstrate the speed of reduction and the type (nanoplatelets) of gold products obtained. After 4 hours, most of the gold has been reduced and the nanoplatelets settled in the vial.

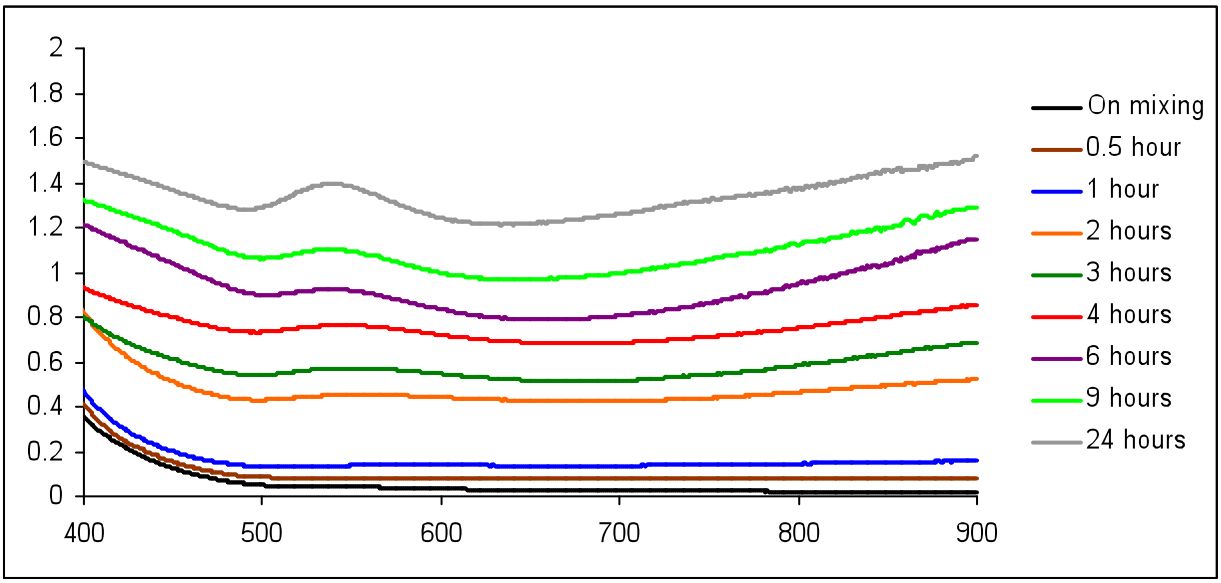


Figure S8 UV-Visible kinetic of gold reduction with polymer **2** at pH = 8 (with a ratio citrate to gold equal to 1.5). The vertical spectra from 0-2 hours may be directly compared, The remaining spectra were amplified due to successive increasing dilution factors. Gold products include some nanoplatelets but also nanoparticles, as evidenced by the SPR absorbance at 530 nm.

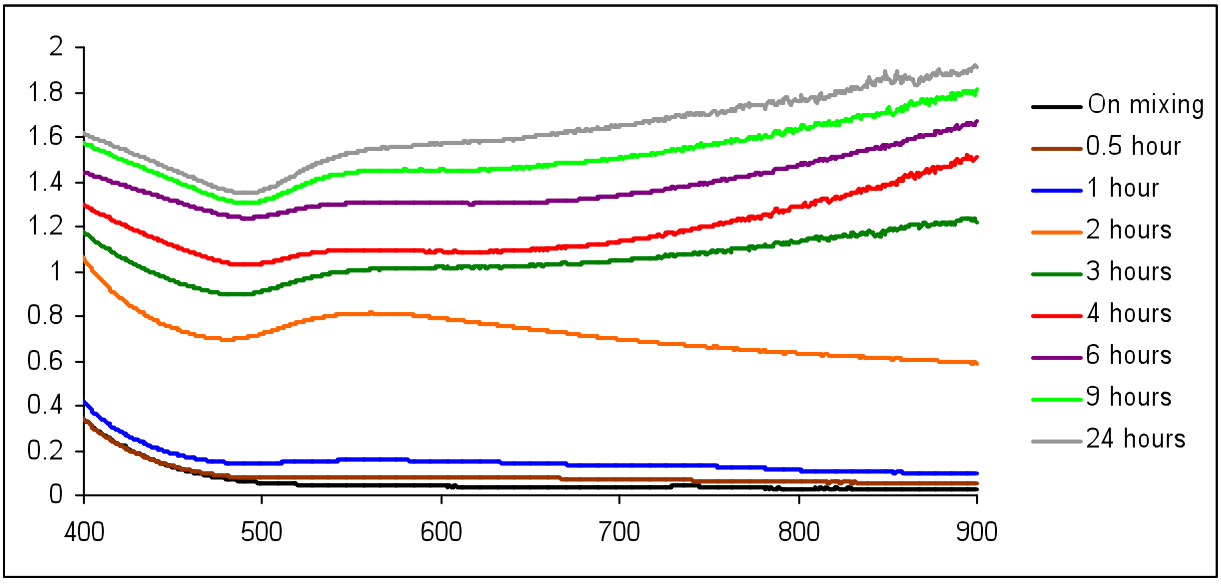


Figure S9 UV-Visible kinetic of gold reduction with polymer **2** at pH = 9 (with a ratio citrate to gold equal to 1.5). The 4 first spectra are directly comparable, the remainder are in arbitrary units due to successive increasing dilution factors.

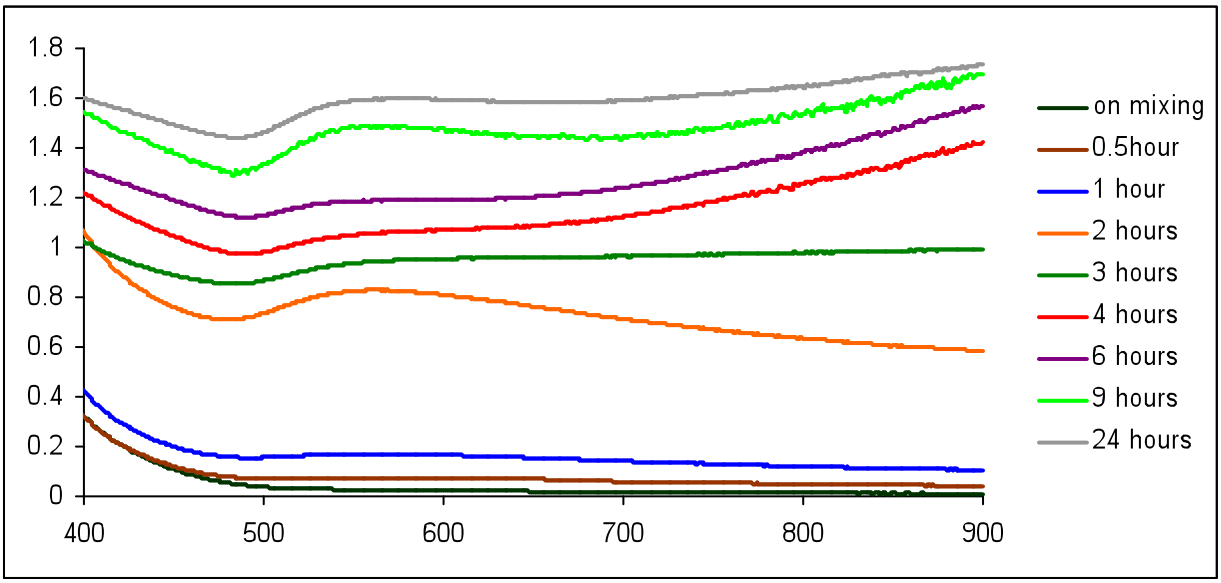


Figure S10 UV-Visible kinetic of gold reduction with polymer **2** at pH = 10 (with a ratio citrate to gold equal to 1.5). The 4 first spectra are directly comparable (from mixing to 2 hours) and show the speed of reduction, while the remainder are in arbitrary units (due to successive increasing dilution factors).