Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.
This journal is © The Royal Society of Chemistry 2023

Supporting information

Red Light-Triggerable Nanohybrid of Graphene Oxide, Gold Nanoparticles and thermo-responsive Polymer for combined Photothermia and Drug Release Effects

Grazia M. L. Consoli [a,b], Ludovica Maugeri[c], Giuseppe Forte[c], Gianpiero Buscarino[d], Antonino Gulino[e], Luca Lanzanò[f], Paolo Bonacci[g], Nicolò Musso[g] and Salvatore Petralia [a,b,c,h]*

[a] *CNR-Institute of Biomolecular Chemistry, Via Paolo Gaifami 18, 95126 Catania, Italy*

[b]*CIB-Interuniversity Consortium for Biotechnologies U.O. of Catania, Via Flavia, 23/1, 34148 Trieste, Italy*

[c]*Department of Drug and Health Sciences, University of Catania, Via Santa Sofia 64, 95125 Catania, Italy*

[d] *Department of Physic and Chemistry, University of Palermo, Via Archirafi 36, Palermo, Italy.*

[e]*Department of Chemical Science, University of Catania, and I.N.S.T.M. UdR of Catania, Via Santa Sofia 64, 95125 Catania, Italy*

[f] *Department of Physic and Astronomy "Ettore Majorana", University of Catania, Via S. Sofia 64, 95123 Catania, Italy*

[g] *Department of Biomedicals and Biotechnologies Sciences, University of Catania, Via S. Sofia 97, Catania, Italy*

[h]*NANOMED - Centro di ricerca in Nanomedicina e Nanotecnologia Farmaceutica, Catania (Italy)*

C**ontents**

Figure S1. FTIR spectrum of GO and PNM.

Figure S2. Representative AFM images of GO-Au nanosystem on MICA substrate.

Figure S3. Representative AFM images of GO-Au-PNM nanosystem on MICA substrate.

Figure S4. DLS measurements at 25°C of GO, GO-Au and GO-Au-PNM dispersion in deionized water.

Figure S5. DLS measurements at different temperature for water dispersion of GO-Au and GO-Au-PNM at pH 5.0.

Figure S6. Photothermal time constant (τ_s) calculation at 0.5 and 0.8 W laser power (680 nm).

Figure S7. Photothermal cycles for GO-Au-PNM/Curc, laser 532 nm (power 0.2 W, 200 μL) and photothermal time constant (τ_s) calculation.

Figure S8. Photothermal cycles for GO-Au-PNM/Curc, laser 405 nm (power 0.2 W, 200 μL) and photothermal time constant (τ_s) calculation.

Figure S9. Thermal release of Curc from GO-Au-PNM/Curc at 37°C: optical absorption spectra of supernatant and absorbance value (433 nm) overtime.

Figure S10. Au-PNM-Curcumin model in vacuo (left) and soaked with water molecules (right).

Table S1. Ordinary one-way ANOVA with Tukey's Multiple comparison test

Table S2 Eint (kcal/mol) values calculated for the five conformations at 315 K and 298 K

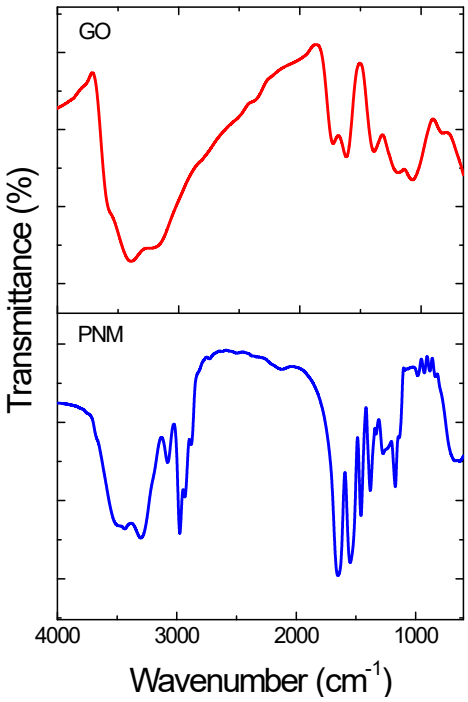

Figure S1. FTIR spectrum of GO and PNM.

FTIR spectra for PNM report the following diagnostic peaks: 3290 cm^{-1} (N-H, stretching), 2971.2 cm^{-1} (C-H, stretching), 1655.2 cm-1 and 1542.3 cm^{-1} (C=O stretching, amide I and II), 1378.6 cm^{-1}, (C-H, bending). FTIR peaks for GO sheets were: 3385.5 cm^{-1} (O-H stretching), 3187.1 cm^{-1} (C-H stretching, 1726.2 cm^{-1} (C=C, stretching), 1610.3 cm^{-1} (CO, stretching) and 1070.2 cm^{-1} (C=O, bending).

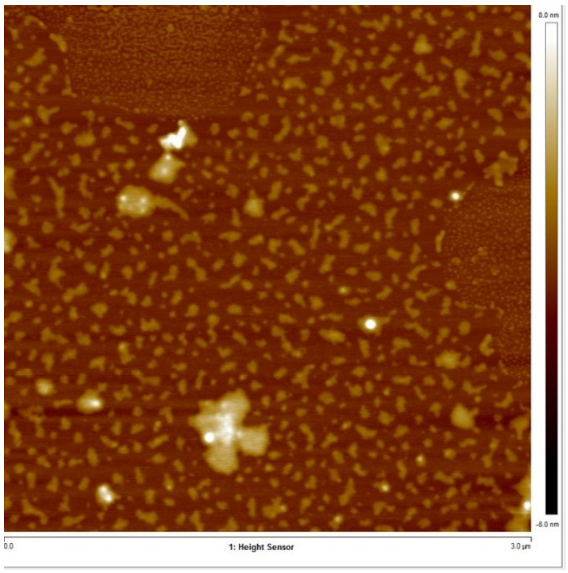

Figure S2. Representative AFM images of GO-Au nanosystem on MICA substrate, full scan image 3 × 3 µm.

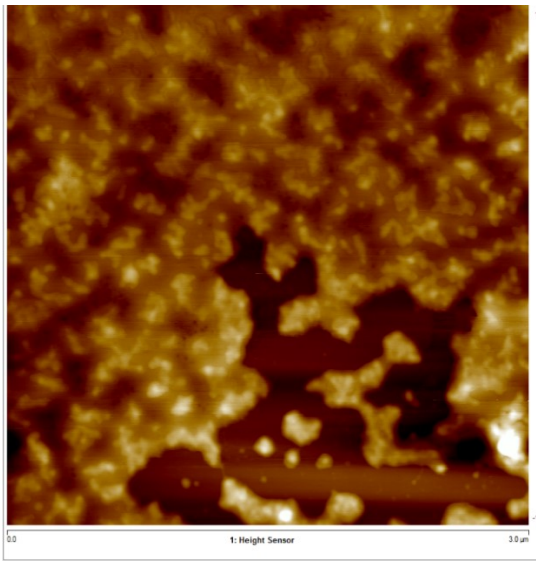

Figure S3. Representative AFM images of GO-Au-PNM nanosystem on MICA substrate, full scan image 3 × 3 µm.

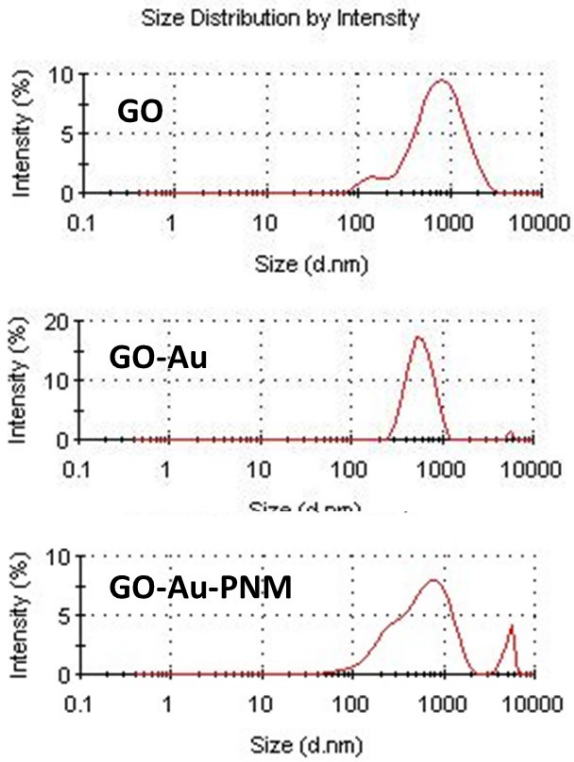

Figure S4. DLS measurements at 25°C of GO, GO-Au and GO-Au-PNM dispersion in deionized water.

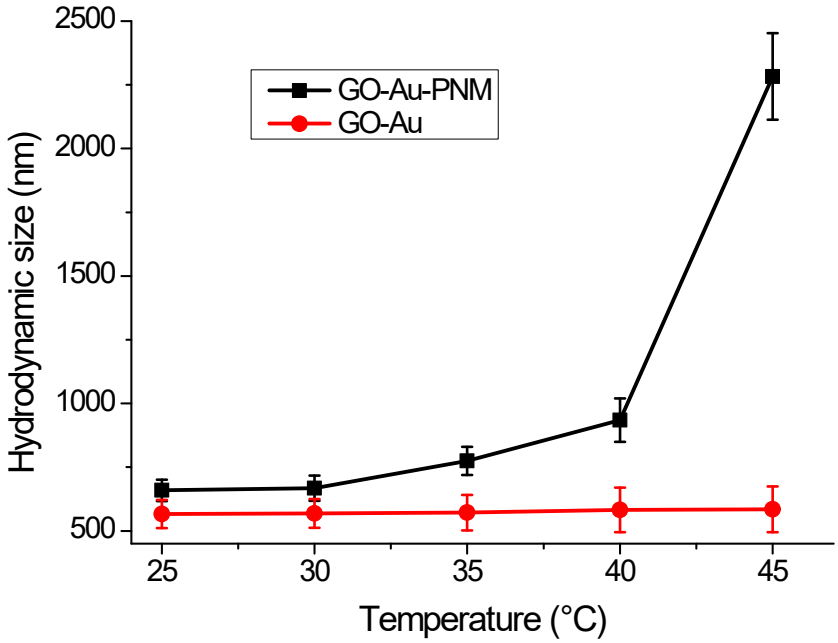

Figure S5. DLS measurements at different temperature for water dispersion of GO-Au and GO-Au-PNM at pH 5.0.

Photothermal measurements

Photothermal properties of GO-Au-PNM nanosystem were investigated by irradiating a glass tube (diameter 3 mm) containing various amount of GO-Au-PNM dispersion. A volume of 200 µL of GO-Au-PNM dispersion was irradiated with a CW laser 680 nm (power 500 mW and 800mW) for 10 minutes. We used the Flirck infrared thermal imaging camera to measure the temperature of solution every 10 seconds, during the heating and cooling processes. Photothermal conversion efficiency (η) of GO-Au-PNM was calculated according to equation (1) introduced by Roper[1].

$$\eta = \frac{hA\left(T_{max} - T_{surr}\right) - Q_{Dis}}{I(1 - 10^{-A})} \qquad (1)$$

Where T_{max} and T_{surr} represents the max photothermal temperature and the ambient temperature respectively. The absorbance (A) at 680 nm is 0.9.

Then, equations (2) and (3) were introduced to obtain unknow hA.

$$\Theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \qquad (2)$$

$$\tau = \frac{M_D C_D}{hA} \qquad (3)$$

where M_D and C_D are the mass of water (0.1 g) and heat capacity (4.2 J g^{-1}) of water, respectively, and τ_s is the time constant.

The time constant τ_s was calculated by the equation (4).

$$t = -\tau(ln\Theta)$$

Laser Power (W)	T max (°C)	T envir. (°C)	Time constant τ (s)	Photothermal conversion efficiency (η)
0.5	45.1	25	117.1	16 %
0.8	54.7	25	114.1	15.5 %

[1] Roper, D. K.; Ahn, W.; Hoepfner, M. *J. Phys. Chem. C* **2007**, *111* (9), 3636-3641

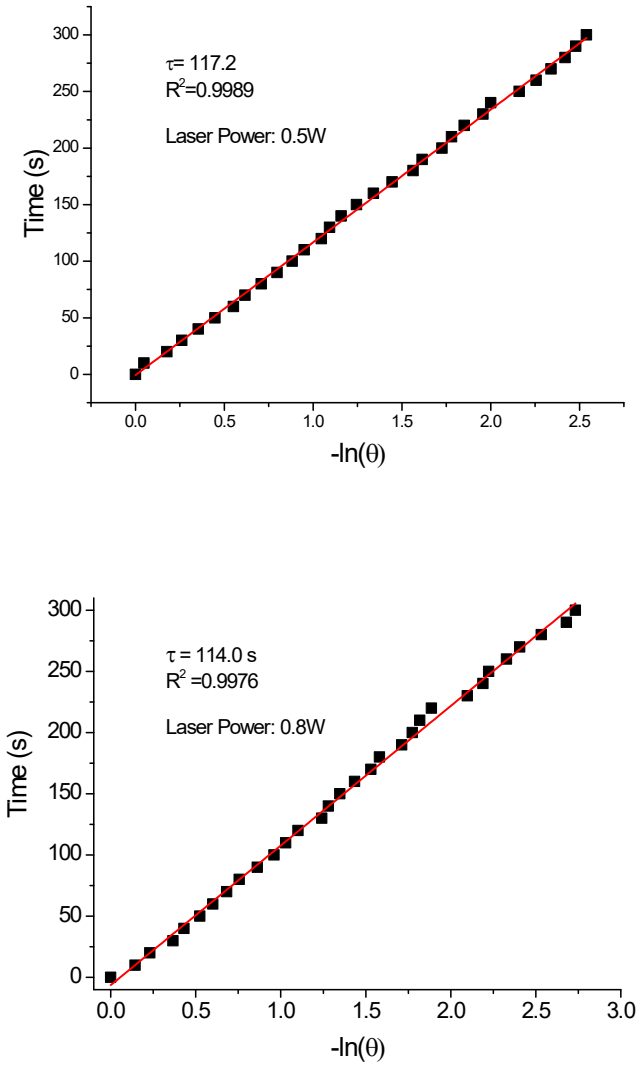

Figure S6. Photothermal time constant (τ_s) calculation at 0.5 and 0.8 W laser power (680 nm).

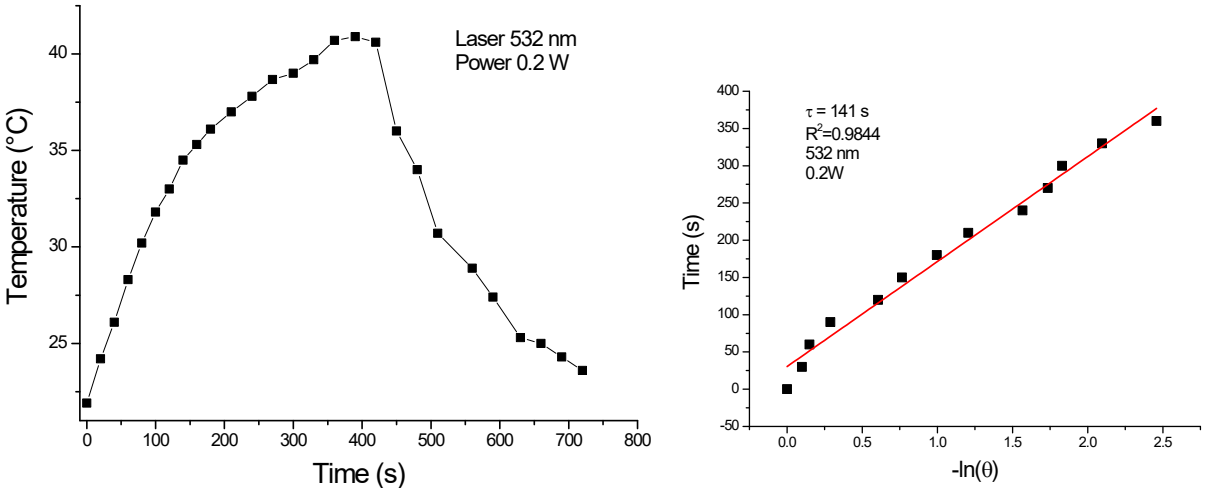

Figure S7. Photothermal cycles for GO-Au-PNM/Curc, laser 532 nm (power 0.2 W, volume 200 µL) and Photothermal time constant (τ_s) calculation.

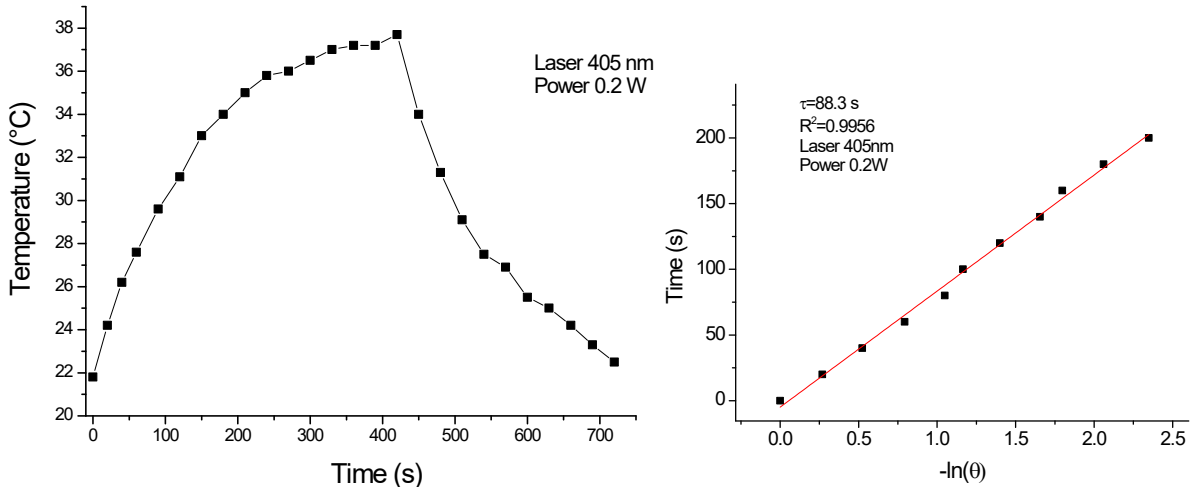

Figure S8. Photothermal cycles for GO-Au-PNM/Curc, laser 405 nm (power 0.2W, volume 200 µL) and Photothermal time constant (τ_s) calculation.

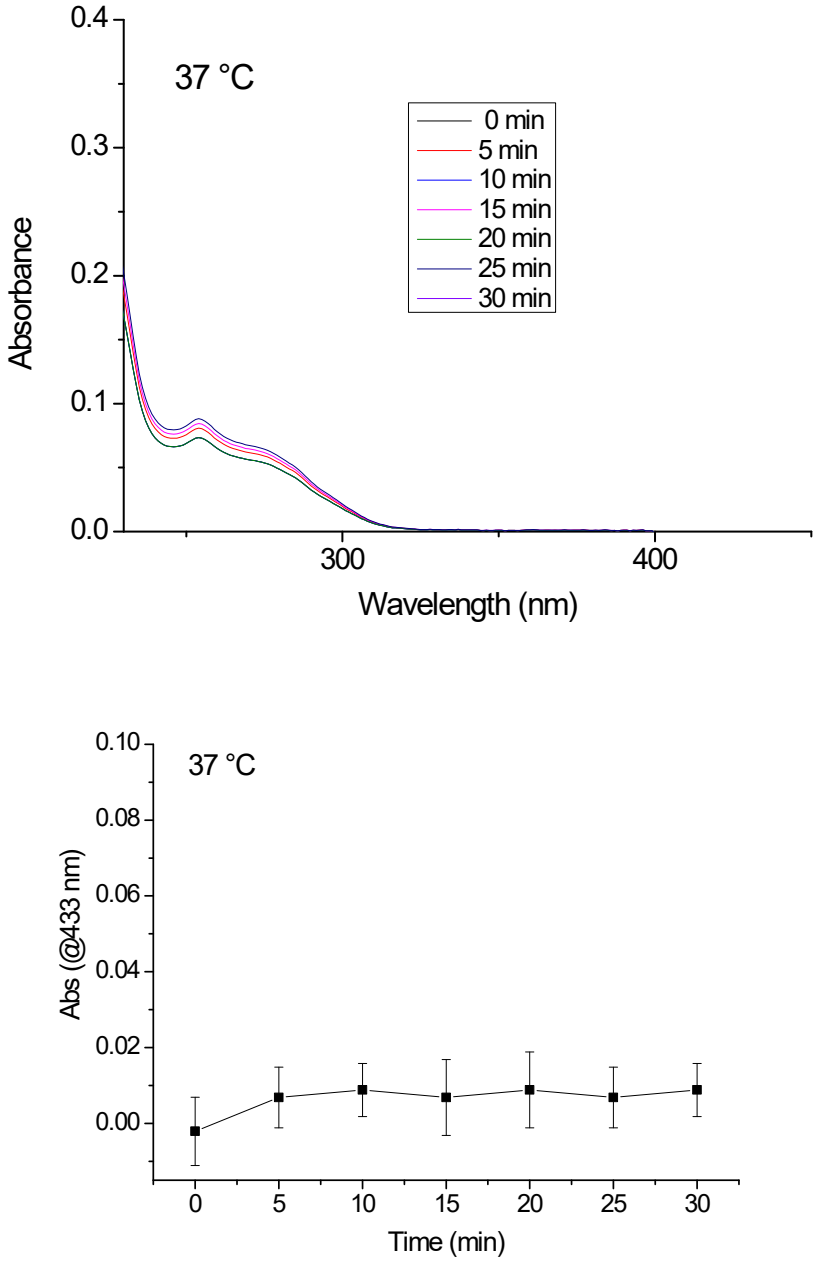

Figure S9. Thermal release of Curc from GO-Au-PNM/Curc at 37 °C: (top) optical absorption spectra of supernatant and (bottom) absorbance value (433nm) overtime.

Table S1: Ordinary one-way ANOVA with Tukey's Multiple comparison test

Tukey's multiple comparisons test	**Mean Diff-**	**95,00% CI of diff.**	**Significant**	**Summary**	**Adjusted P Value**
CTRL vs. 4 µg	15.59	-2.389 to 33.58	No	ns	0.1079
CTRL vs. 0.4 µg	6.106	-11.88 to 24.09	No	ns	0.8399
CTRL vs. 0 04 ng	0.1213	-17.86 to 18.10	No	ns	>0.9999
CTRL vs. 0 004 ng	3.070	-14.91 to 21.05	No	ns	0.9846
4 µg vs. 0.4 µg	-9.489	-29.78 to 10.,80	No	ns	0.6269
4 ug vs. 0 04 ng	-15.47	-35.76 to 4.815	No	ns	0.1882
4 ug vs. 0 004 ng	-12.52	-32.81 to 7.763	No	ns	0.3689
0.4 ug vs. 0 04 ng	-5.984	-26,27 to 14.30	No	ns	0,.8962
0.4 ug vs. 0 004 ng	-3.036	-23.,32 to 17.25	No	ns	0,9906
0 04 ng vs. 0 004 ng	2.948	-17.34 to 23.24	No	ns	0.9916

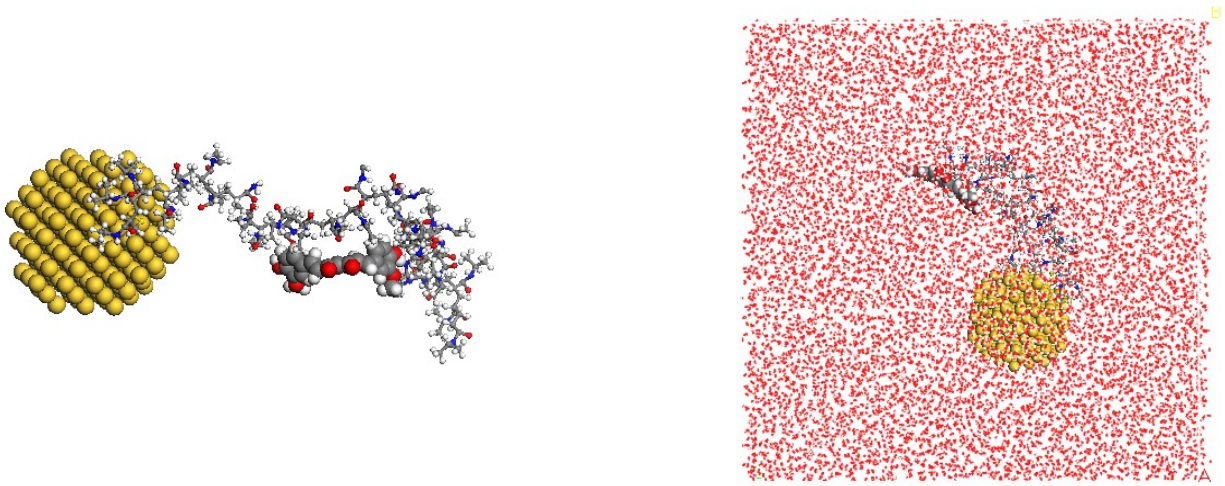

Figure S10. Au-PNM-Curcumin model in vacuo (left) and soaked with water molecules (right). Au Nanoparticle and Curcumin are reported in CPK representation, PNIPAM is illustrated in ball and stick representation.

Table S2 Eint (kcal/mol) values calculated for the five conformations at 315 K and 298 K

Conformation	**Eint (kcal/mol) 315 K**	**Eint (kcal/mol) 298 K**
S01	- 54.21	- 37.06
S02	- 48.69	- 40.33
S03	- 47.09	- 33.82
S04	- 25.18	- 35.47
S05	- 21.78	- 33.40