Supplementary data

Supramolecular Hybrid Assemblies based on Gold Nanoparticles, Amphiphilic Cyclodextrin and Porphyrins with Combined Phototherapeutic Action

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The Supplementary Information includes:

1. Supporting Information, Fig. S1-S3.

2. Experimental Details.

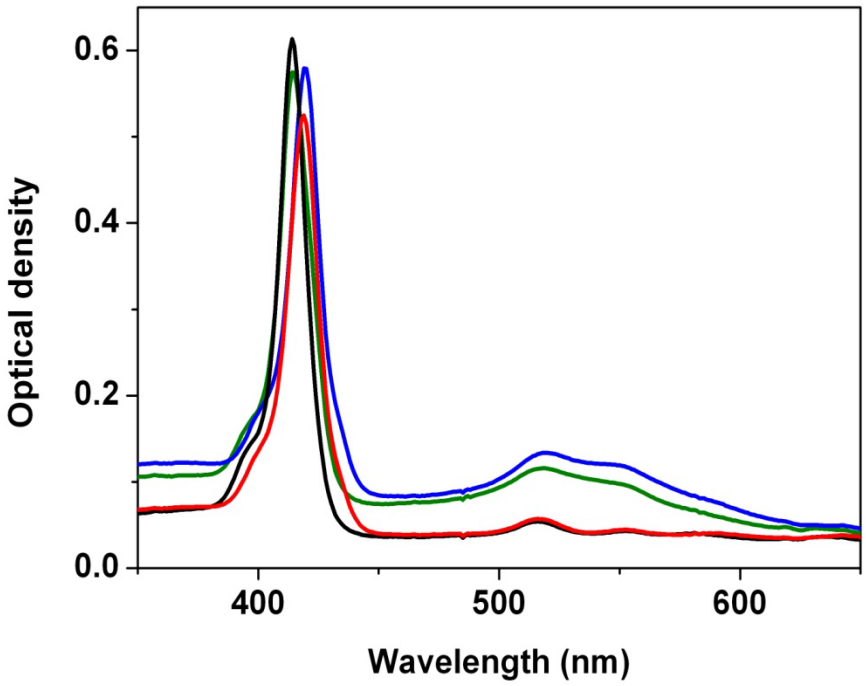

Fig. S1: UV-Vis spectra (cell path, d= 0.2 cm) of $TPPS_4$, (black trace), AuNPs+$TPPS_4$ (green trace), SC6NH2/$TPPS_4$ (red trace) and AuNPs@SC6NH2/$TPPS_4$ (blue trace) nanoassemblies in aqueous solution at high SC6NH2/$TPPS_4$ load ([AuNPs]≅ 1 μM, [SC6NH2]= 50 μM, [$TPPS_4$]= 5 μM).

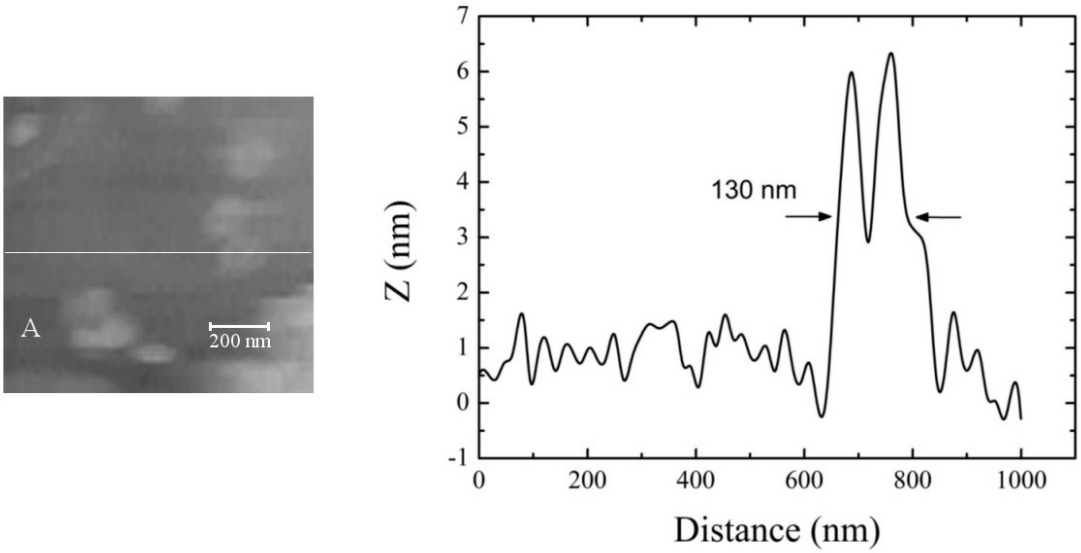

Fig. S2: SNOM topography and the correspondent line profile extracted along the marked trace of AuNPs@SC6NH2/$TPPS_4$ nanoassemblies. The analyzed sample was casted from 30 times diluted solution of nanoassemblies at low SC6NH2/$TPPS_4$ load up to final concentrations [AuNPs]≅0.03 μM, [SC6NH2]= 2.7 μM, [$TPPS_4$]= 0.013 μM. The structures have a dimension of about 150 nm and a high of about 7-10 nm.

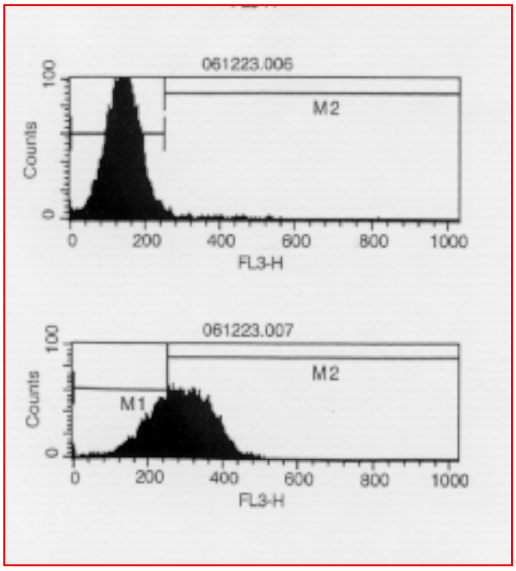

Fig. S3: Flow cytometry analysis for detection of $TPPS_4$ in HeLa cells after treatment with $TPPS_4$ free (upper) and with AuNPs@SC6NH2/$TPPS_4$ system at low SC6NH2/$TPPS_4$ load. Cells were analyzed after overnight incubation. Solid peaks represent the emission of internalized $TPPS_4$ (red emission). The lines designated as M1 and M2 indicate the boundaries among the peaks of negative and positive cells, respectively.

2 Experimental details

Dynamic Light Scattering: A polarized He-Ne laser (632.8 nm) with a power of 15 mW was used as source impinging to the sample; the collected scattered light was sent to a Malvern 4700 submicrometer particle analyzer system to obtain the scattered intensity autocorrelation function. Using the hypothesis that the scattered electric field obeys a Gaussian statistics,[1] the normalized scattered electric field correlation function g_1(Q, t), defined as $g_1(Q,t) = \frac{\langle E^*(Q,0)E(Q,t)\rangle}{\langle I(Q)\rangle}$ is obtained (Q being the exchanged wavevector equal to $(4\pi n/\lambda)\sin(\theta/2)$, θ the scattering angle, n the refractive index of the solution, and λ the wavelength of light in a vacuum).

For diffusing monodisperse spherical scatterers with radius *R*, the normalized scattered electric field autocorrelation function takes a simple exponential form, $g_1(Q, t)= \exp(-\Gamma(Q)t)$. Under the condition QR< 1 (and for rigid scatterers also for QR>1), Γ is related to the collective diffusion coefficient, *D*, by the relation $\Gamma=DQ^2$, from which the hydrodynamic radius, R_H, can be calculated by using the Einstein-Stokes relation

$R_H = \frac{k_B T}{6\pi\eta D}$ (where k_B is the Boltzmann's constant, T the absolute temperature, and η the solvent viscosity). **For polydisperse scatterers, the size distribution was obtained through the Laplace inversion of the scattered electric field correlation function,** $g_1(t) = \int \tau A(\tau) \exp(-t/\tau) d(\ln \tau)$ **(with τ = 1/(*DQ*^{2})), by using the CONTIN algorithm.[1] By taking into account the non-normalized form factor of scatterers with radius R_H through the Mie theory, it is possible to estimate the mass fraction of each species starting from its spectral amplitude τA(τ).**

(1) B. J. Berne, R. Pecora, R. *Dynamic Light Scattering*; Wiley-Interscience: New York, 1976