Multifunctional core-shell hybrid nano-composite made by

Pickering emulsions: a new design for therapeutic vectors.

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Figure S1A: Top: NMR spectrum of Dioctyl Terephthalate in deuterated methanol. Bottom: NMR spectrum of the filtrate of the release solution, after a 7 day exposition of as made particles in fresh PBS. For DOT, the integration of the aromatic peak (at 8.1 ppm) is the same than the integration of the peak at 4.3 ppm due to the resonance of the closest methylene protons to the oxygen of the ester bond. After release, the intensity of the methylene protons has decreased in comparison to aromatic protons. The hydrolysis of the ester took place. The protons of residual octanol have a chemical shift below 4 ppm. DOT, half-hydrolyzed DOT (i.e. mono-octyl terephthalate); and fully hydrolyzed DOT (i.e. terephthalate dianion) are present in the filtrate.
Figure S1B: (blue) FTIR spectrum of commercial terephthalaldehyde centered onto carbonyl vibration bands. (red) FTIR spectrum of dioctyldialdimine terephthalate obtained after reacting for one hour 17 mg of terephthalaldehyde (one equivalent) with 33 mg of octylamine (two equivalents) in 1 mL of methanol.
Figure S1C: Liquid $^1$H-NMR spectrum of di-tetradecylamide terephthalate obtained by reacting 0.256 g of terephthaloyl chloride dissolved in 5 mL of DMSO, with 1.076 g of tetradecylamine in 20 mL dissolved at 70°C in DMSO. NMR acquisition was performed in deuterated methanol-d4.

Integrations: a) 0.9 ppm – 6, b) 1.29 ppm- 52, c) 1.63 ppm- 4, d) 2.9 ppm- 3.62, d’) 2.66 ppm- 0.66, e) 3.31 ppm- solvent, f) 4.2 ppm- 0.67, g) 4.86 ppm-water, h) 7.9 ppm- 3.02.

One peak only can be observed at 7.9 ppm (aromatic protons): all protons of aromatic ring are equivalent (no mono amide function in this product).

d’) signal and the excess of proton of b) signal comes from non-reacted amine and d) from amide. As a consequence, the reaction yield can be estimated from the ratio of relative integration of peaks d/(d+d’), that is $\frac{3.62}{(3.62+0.66)} = 0.84$
Figure S2: A) Thermogravimetric Analysis of as made MDot particles. B) TGA of MDot particles after DOT release
Figure S3: SAXS pattern of as-made MDOT particles.
Figure S4: Magnetic hyperthermia measurements on a solution of the maghemite NPs dispersed in water at [Fe]=20mM. Temperature was probed with a fluoroptic fiber thermometer and recorded every 0.7 s. The temperature curves (example shown on the top graph) provide with the plateau temperature and the Specific Absorption Rate (SAR, expressed in W/g), calculated as follows from the initial slope (dT/dt) (in K/s):

$$SAR = \frac{CV_s \frac{dT}{m}}{dt}$$

with $C_{\text{water}}= 4185 \text{ J.L}^{-1}\text{K}^{-1}$ the volume specific heat capacity of the sample, $V_s$ the sample volume and $m$ the mass of iron in the sample.
Figure S5: TEM picture of a as made pickering vector obtained from Pickering emulsion after (top) ultrasound treatment, (bottom) after filtration treatment.
Figure S6: Terephthalate calibration curve for UV-Vis analyses plotting Optical Density versus DOT concentration in mol.L$^{-1}$ in PBS.
Figure S7: Model prodrug release reference test for DAI and DOT in PBS without maghemite. As we can see, DOT does not hydrolyze in such conditions. DAI on the other hand is very quickly hydrolyzed (we stopped this experiment after one day). Amide bonds being much more stable than ester bonds at pH 7.4, we did not test DI molecules in this way.