Controlled Anchoring of Iron-Oxide Nanoparticles on Polymeric Nanofibers: Easy Access to Core@Shell Organic-Inorganic Nanocomposites for Magneto-Scaffolds

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Table S1. Reaction conditions for the propargylation of PLA nanofibers. The anionic activation (step 1) and nucleophilic substitution (step 2) were carried out at −50°C under argon atmosphere.

Set of parameters	Et_2O/THF (v:v)[a]	Solvent temperature[a]	Step 1 LDA/time	Step 2 PgBr/time	Grading of fibers' degradation
1	75:25	−20°C	0.125 mL/30 min	0.125 mL/ 1 h	++
2	75:25	−20°C	0.06 mL/30 min	0.06 mL/ 1 h	++
3	95:5	−20°C	0.7 mL/30 min	0.7 mL/ 1 h	+
4	100:0	−20°C	0.5 mL/15 min	0.5 mL/ 15 min	none

[a] Volume of solvent mixture set to 100 mL for all experiments.
[b] Temperature of the solvent mixture when fibers are immersed in the reaction medium

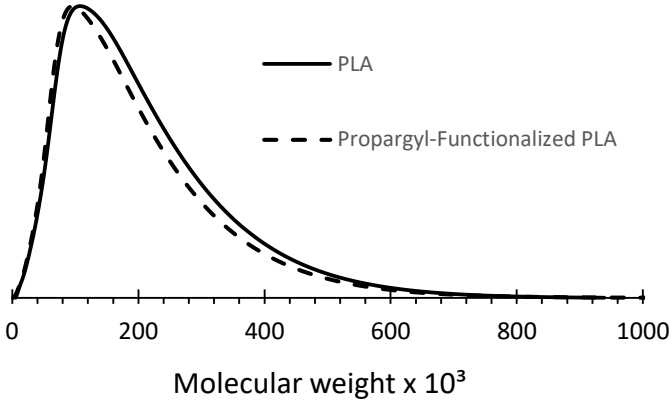


Figure S1. SEC curves of the pristine PLA (bold line) and of the propargylated PLA (dashed line) (Table S1 – entry 4).

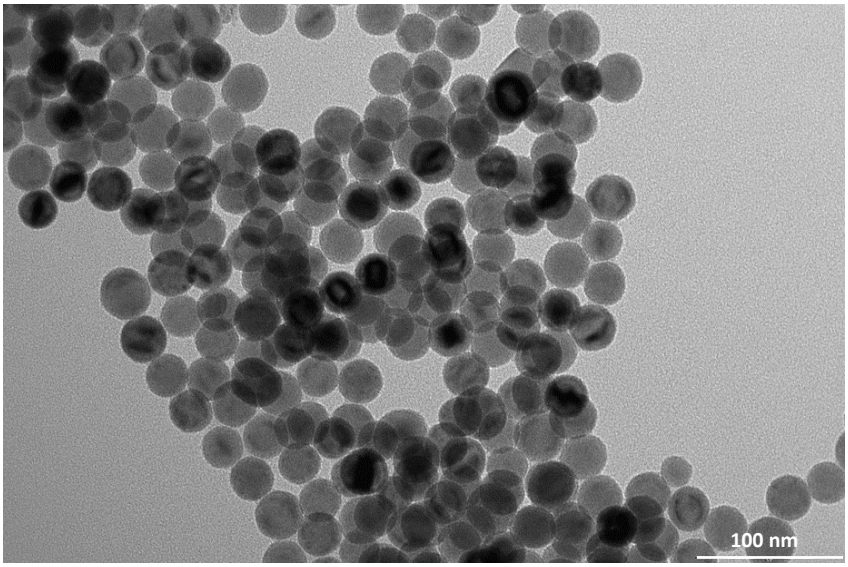


Figure S2. TEM image of oleic acid functionalized SPIONs.

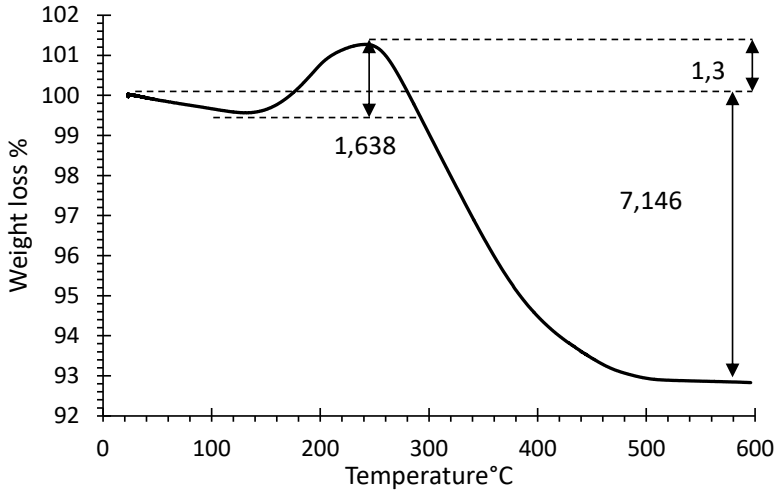


Figure S3. Thermogravimetric analysis of thiol-functionalized SPIONs.

Calculation of the grafting density of the thiol-ligand at the surface of the SPIONs:

From the TEM analysis, the particle diameter is 18 nm.

Thus, the surface area of a single particle is $4 \times \pi \times 9^2 = 1018$ nm^2

and the volume of a single particle is $4/3 \times \pi \times 9^3 = 3054$ nm^3

The density of iron oxide is ~ 5.2 g/cm^3

Thus, the mass of a single particle is ~ 1.59×10^{-17} g

From the TGA results, the weight of ligand coated on a single particle is $(1.59 \times 10^{-17}$ g).(7/93)

$= 1.20 \times 10^{-18}$ g

The molecular weight of the thiol- ligand is 282.38 g/mol.

Hence, the number of ligands in one particle is

$(1.20 \times 10^{-18}$ g) x $(6.02 \times 10^{23})/(282.38$ g/mol) ≈ 2550

This implies that the grafting density is equal to 2550/1018 ≈ 2.5 molecules/nm^2

Table S2. Reaction conditions and results for strategy 1 (Scheme 2): thiol-yne photo-addition of SPIONs-SH on propargylated PLA nanofibers.[a]

Entry	Estimated quantity of thiol functions (nmol)	Irradiation time (min)	Presence of TCEP (nmol)	Grading for the presence of SPIONs aggregates[b]	EDXS analysis of relative Fe /P / S content [c]
1	62.5	5	no	1	nd
2	62.5	10	no	2	nd / 0.15 / 0.13
3	134	10	no	4	nd/ 0.31 / 0.25
4	134	10	134	3	nd / 0.14 / 0.14

[a] All experiments were performed using freshly prepared functionalized SPIONs, and 1 eq. of DMPA with respect to thiol)
[b] Grading corresponds to 0: none 1:rare ; 2:few ; 3:some ; 4:many
[c] Mean atomic percentages determined by EDX analyses on the fibers, in areas free of aggregates (n=2; nd = not detected); the lack of Fe detection attests of the absence of NPs.

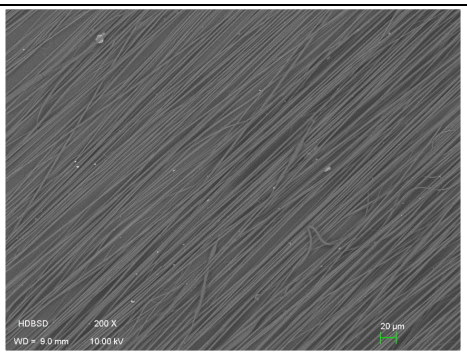
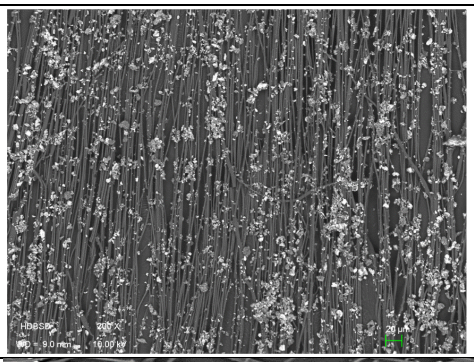
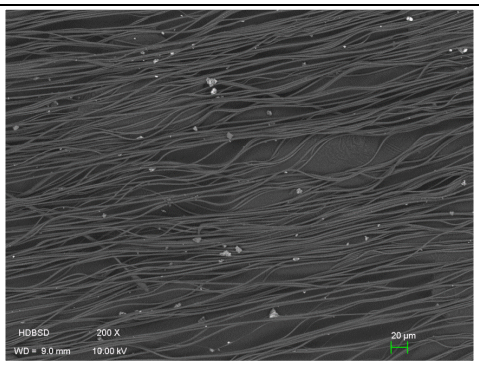
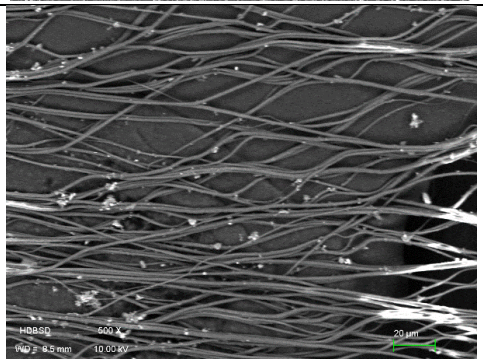
Entry of Table 1	SEM images	Entry of Table 1	SEM images
1		**3**	
2		**4**	

Figure S4. SEM images corresponding to the reaction conditions of Strategy 1, as listed in Table S2.

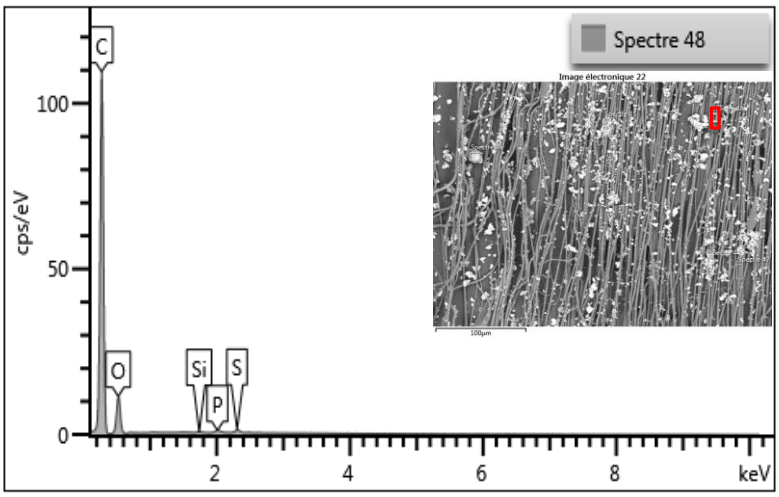


Figure S5. EDXS analyses corresponding to the photoaddition of thiol-functionalized SPIONs at the surface of propargylated PLA nanofibers (Strategy 1), with the highest concentration of SPIONs and without TCEP (Table S2 entry 3). The detection of P and S in a zone without any visible aggregates can be explained by the coupling of residual "free" thiol-phosphonic ligands present in the SPION suspension with the propargylated surface.

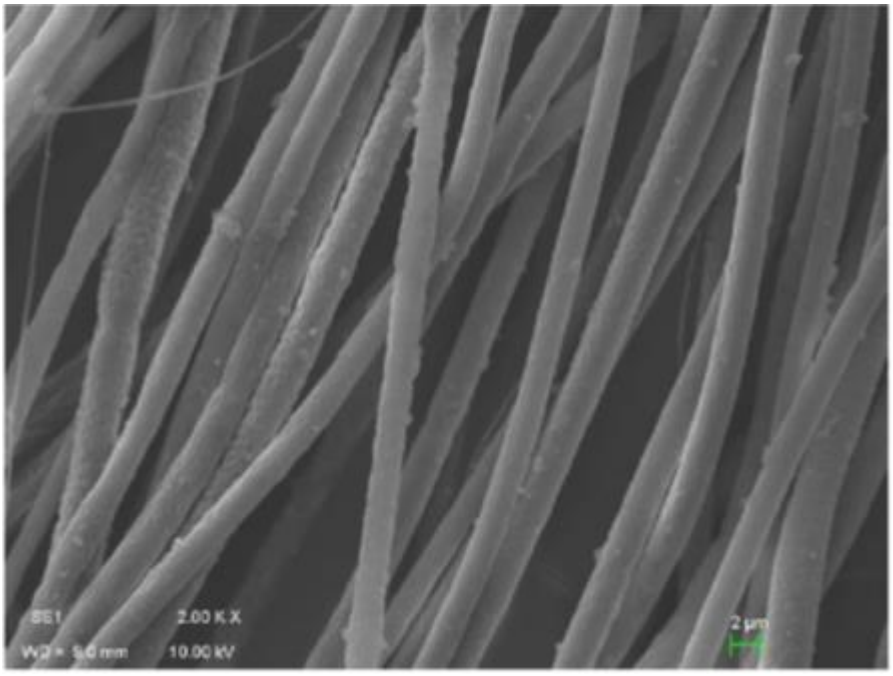


Figure S6. SEM image at high magnification of PLA@SPIONs prepared using strategy 2.

Table S3. The atomic percentage of elements presented on the surface of PLA@SPIONs nanofibers before and after immersion in PBS solution measured by EDXS analysis.

	Samples	
Elements	PLA@SPIONs (atomic %)	PLA@SPIONs + 72 h in PBS solution (atomic %)
C	69.05	67.73
O	27.93	27.38
P	0.11	0.81
S	0.09	0.51
Fe	2.83	2.69
Na		0.81
Cl		0.69
total	100	100

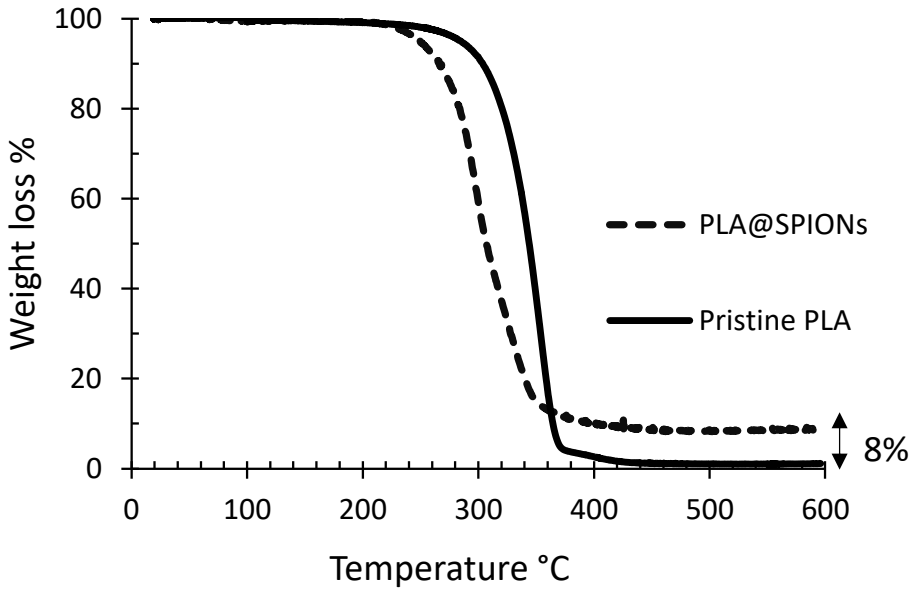


Figure S7. Thermogravimetric analysis of Pristine PLA and PLA@SPIONs.

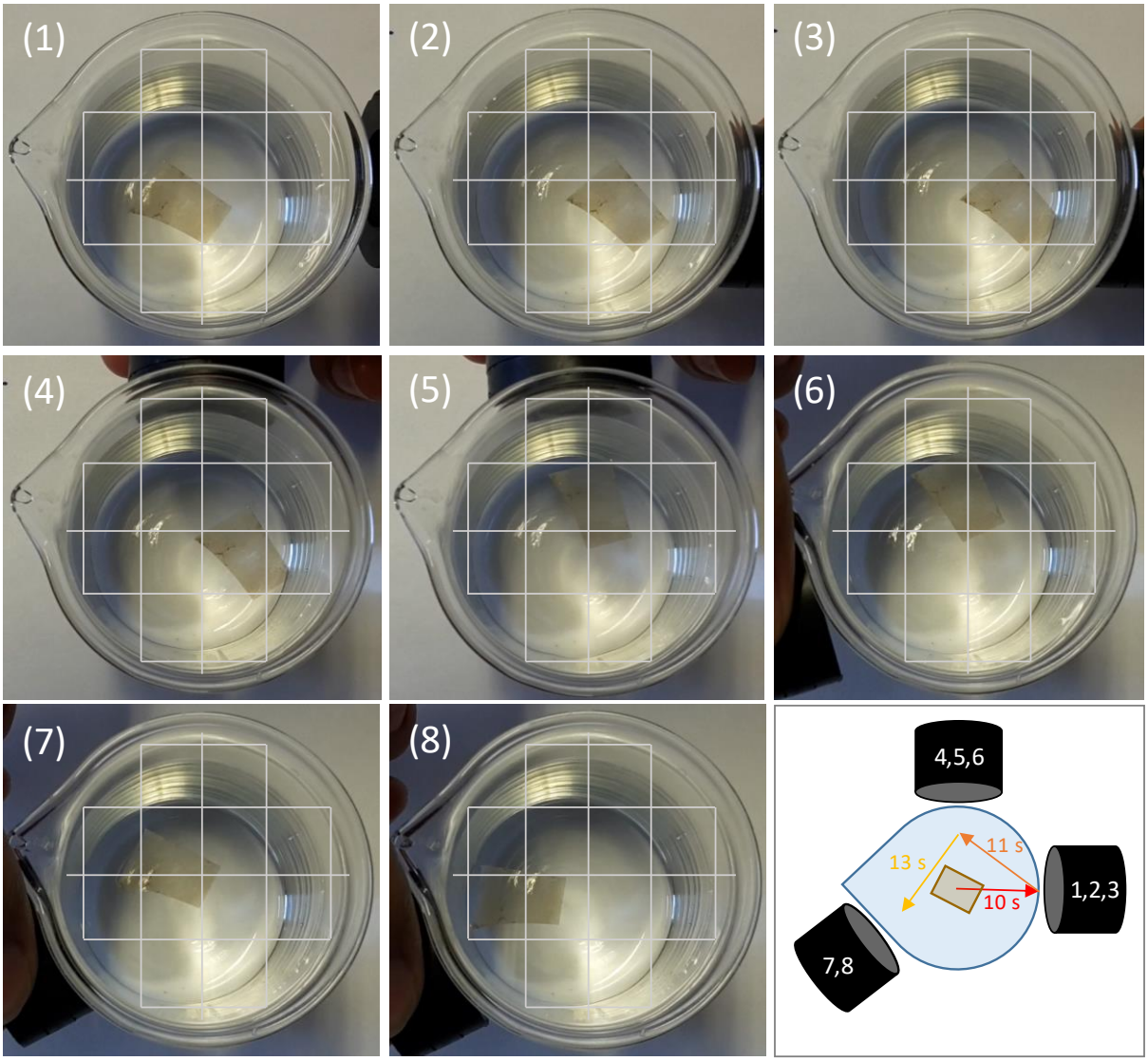


Figure S8. Displacement of PLA@SPIONs nanofibers supported on a glass slide (strategy 2) under the influence of a magnet (Neodynium-based magnet 20X10 mm, 1.08-1.25 T). The sketch provided on the bottom right summarizes the successive positions of the magnet (black cylinder), the induced displacement of the SPION-functionalized fibers supported on a glass slide (colored arrows), and the time needed for each displacement (see Movie S1 for the complete motion).

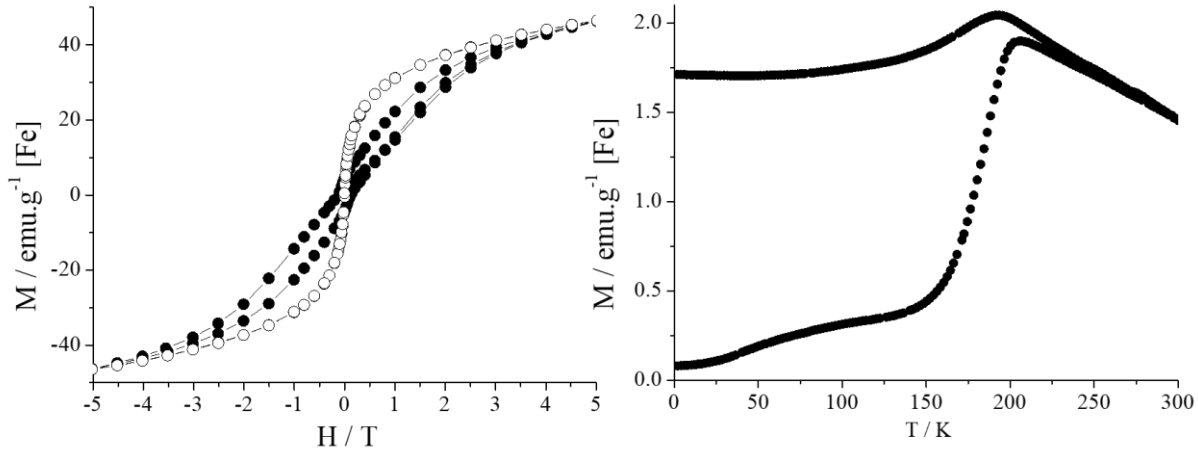


Figure S9. left) Field dependence of the magnetization for non-grafted SPION at 2.5 K (•) and at 300 K (○); right) FC/ZFC curves for non-grafted SPION performed with an applied magnetic field of 0.005 T.



Figure S10. The PLA@SPIONs nanofibers film used in MRI imaging (top view).

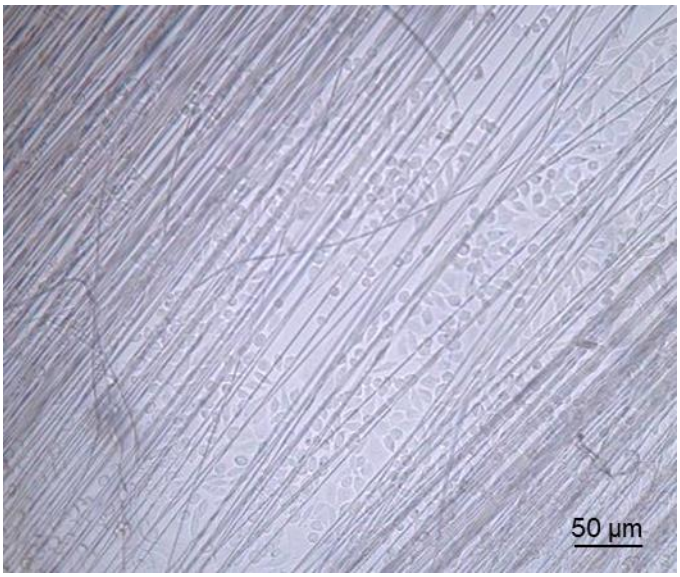


Figure S11. Optical microscopy picture of L929 murine fibroblast cells cultured on PLA@SPIONs nanofibers. The presence of cells between the fibers (*i.e*. directly on the glass support) is clearly visible, and illustrates the inadequacy of a cellular assay involving the evaluation of cell proliferation on the modified fibers.