### **Supporting Information**

Double Entrapment of VEGF by PCL nanoparticles loaded into Polyelectrolyte multilayer films

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#### Figure S1.

Build-up of PLL/HA multilayer film (black discs) and nanoparticle deposition (red disc) on a SiO<sub>2</sub> coated crystal followed by QCM (a). The evolution of the normalized frequency  $-\Delta f/v$  as a function of the number of layers of polyelectrolytes and nanoparticles deposited was monitored for the third overtone (15 MHz). To characterize the film at a given step, only the frequency at the end of the rinsing steps following the exposure to polycations or polyanions or nanoparticles were shown on the graph. Kinetic of PCL nanoparticles deposited at on a (PLL/HA)<sub>7</sub> film was followed over 23 hours (red symbol in graph (a) and graph (b)). 600 µL of the nanoparticles were deposited at 0.02 mg/mL with a flow rate of 250 µL/min.



#### Figure S2a.

Typical force curves were recorded on PLL/HA matrix without nanoparticles (a) and with various nanoparticle loadings ( $25\mu$ L (b),  $50\mu$ L (c),  $100\mu$ L (d) and  $200\mu$ L (e)). White circles correspond to experimental data taken from extended force curves and the red lines correspond to the theoretical fitting with Hertz model. The maximal indentation depth measured for a loading force of 4 nN was decreased successively from 550 nm to 250, 180 and 120 nm when (PLL/HA) matrices were incubated with 25, 100 and 200  $\mu$ L of nanoparticles respectively. This decrease of the maximal indentation depth can be related to stiffnening of the matrix elasticity, e.g. an increase of the Young modulus.



#### Figure S2b.

The statistic distribution of Young moduli taken from (PLL/HA) films incubated with increasing nanoparticle concentrations (b, c, d and e) or not (a) was calculated on force-volume images of 1024 force-curves over an area of 40  $\mu$ m × 40  $\mu$ m reported in the insets. The corresponding maps represent the stiffness of the films (dark pixels) and the substrate (white pixel) for a bar-scale in the range of 0 to 50, 100 and 500 kPa. These elasticity maps indicated a homogeneous stiffness of the (PLL/HA) matrices without nanoparticles (a) and with films loaded with increasing nanoparticle volumes : 25  $\mu$ L, 50  $\mu$ L, 100  $\mu$ L and 200  $\mu$ L (b, c, d and e respectively).



# Figure S2c.

The stiffness of the (PLL/HA) films increases linearly with the deposited volume of PCL nanoparticles.



## Figure S3.

HUVEC proliferation on the PLL/HA films loaded with empty nanoparticles (without VEGF) at day 1 and day 3. Addition of nanoparticles improved the proliferation due to stiffness increase. However, the NP loaded multilayers could not sustain cell proliferation due to the absence of VEGF. Cell proliferation was determined by a Resazurin based assay with absorbance readings at 600 nm and reference readings at 690 nm. Positive control corresponds to TCPS surfaces.



# Figure S4.

Expression of PECAM was checked for HUVEC growing on TCPS around PLL/HA (green labelling). PECAM is an indicator of HUVECs activity. Blue and red stainings correspond respectively to DAPI and TRITC-phalloidin.



