# SUPPORTING INFORMATION

## 1. NMR analysis of the synthesized $PLL_{20}$-$g_{3.5}$-$PEG_{2/3.4}$-TG

The synthesized $PLL_{20}$-$g_{3.5}$-$PEG_{2/3.4}$-TG copolymer was analyzed by $^1H$ NMR ($D_20$) and resulted in a copolymer with the following structure: $PLL_{20}$-$g_{4.4}$-$PEG_{2/3.4}$-$TG_{25\%}$.

$^1H$ NMR ($D_2O$) d:
0.83 (TG-peptide, -CH3 valine side chains, d),
1.18-1.48 and 1.48-1.81 (PLL, -$C_\alpha HC_\beta \underline{H_2} C_\gamma \underline{H_2} C_\delta \underline{H_2} C_\varepsilon H_2 NH_2$, m),
1.81-2.48 (TG-peptide, side chains),
2.90 (PLL, -$C_\alpha HC_\beta H_2 C_\gamma H_2 C_\delta H_2 C_\varepsilon \underline{H_2} NH_2$, t),
3.05-3.14 (PLL and TG-peptide, -$C_\alpha HC_\beta H_2 C_\gamma H_2 C_\delta H_2 C_\varepsilon \underline{H_2}$NHCO and side chains, m),
3.28 (mPEG, -$OC\underline{H_3}$, s),
3.60 (mPEG and PEG, -$OC\underline{H_2}C\underline{H_2}$-, m),
4.05 (TG-peptide, -NHCα<u>H</u>CO-, d),
4.21 (PLL and TG-peptide, -NHCα<u>H</u>CO-, m),
4.32 (TG-peptide, -$NHC_\alpha\underline{H}$CO-, t),
4.45 (TG-peptide, -NHCα<u>H</u>CO-, t)

The grafting ratios were calculated from the NMR spectrum. The ratio between $mPEG_{2000}$ and $PEG_{3400}$, to which the TG-peptide has been coupled, was determined from the integral value of the methoxy group of $mPEG_{2000}$ peak at 3.28 ppm and from the integral value of the ethyleneoxide group of both $mPEG_{2000}$ and $PEG_{3400}$ peaks between 3.42-3.73 ppm. Based on the signal from the methoxy group of $mPEG_{2000,}$ the value for one proton of $mPEG_{2000}$ is 0.36. This results in a total integral value for $mPEG_{2000}$ with 45 ethylene oxide units of 64.80 and leaves a signal of 36.03 for the 77 ethylene oxide unit of $PEG_{3400}$. This represents a value for one proton of $PEG_{3400}$ of 0.12. Therefore the proportion of $mPEG_{2000}$ to $PEG_{3400}$ is 0.36 to 0.12 which is a ratio of 3 to 1.

Based on the signal at 0.83 ppm from the four methyl groups of the two valine residues in the TG-peptide and on the signals at 4.05, 4.32 and 4.45 ppm representing six protons from the $C_\alpha H$ groups in the TG-peptide, one proton from the TG-peptide has an integral value of 0.12. This value is the same as that of the $PEG_{3400}$. Therefore, each $PEG_{3400}$ is functionalized with one TG-peptide.

To calculate the ratio between the PEGs and PLL, the integral values from the $C_\beta H_2$, $C_\gamma H_2$ and $C_\delta H_2$ groups of PLL representing 6 protons are used. One proton from PLL is represented by a value of 2.13 and one proton of the PEGs is represented by a value of 0.36 and 0.12. This results in a PLL-PEG grafting ratio of 4.4 to 1.

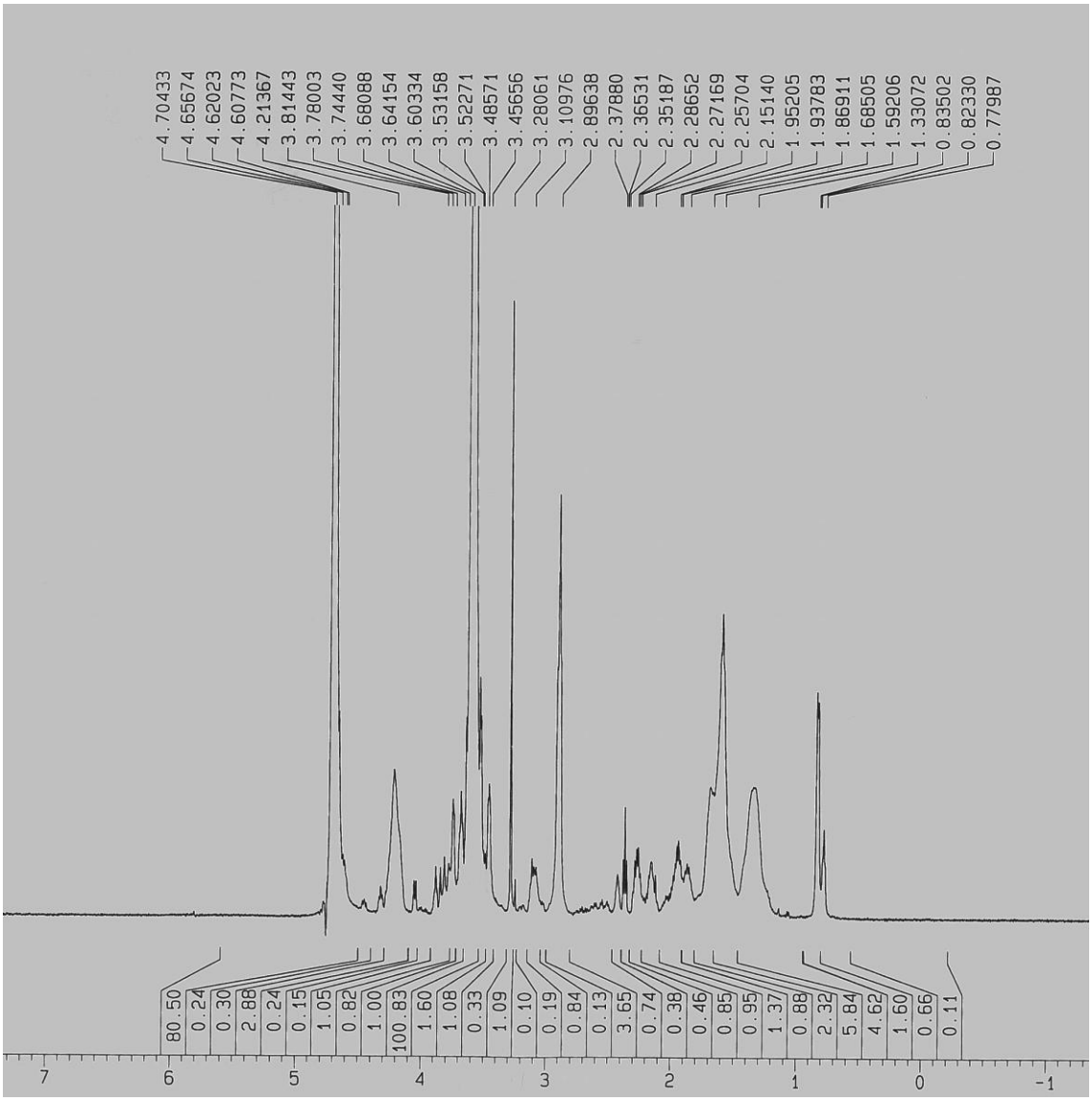


**Figure S1.** NMR of PLL-*g*-PEG-TG.

## 2. *In situ* OWLS monitoring and quantification of PLL-*g*-PEG-TG adsorption on a titanium-coated waveguide and degree of resistance of the polymeric adlayer to serum adsorption.

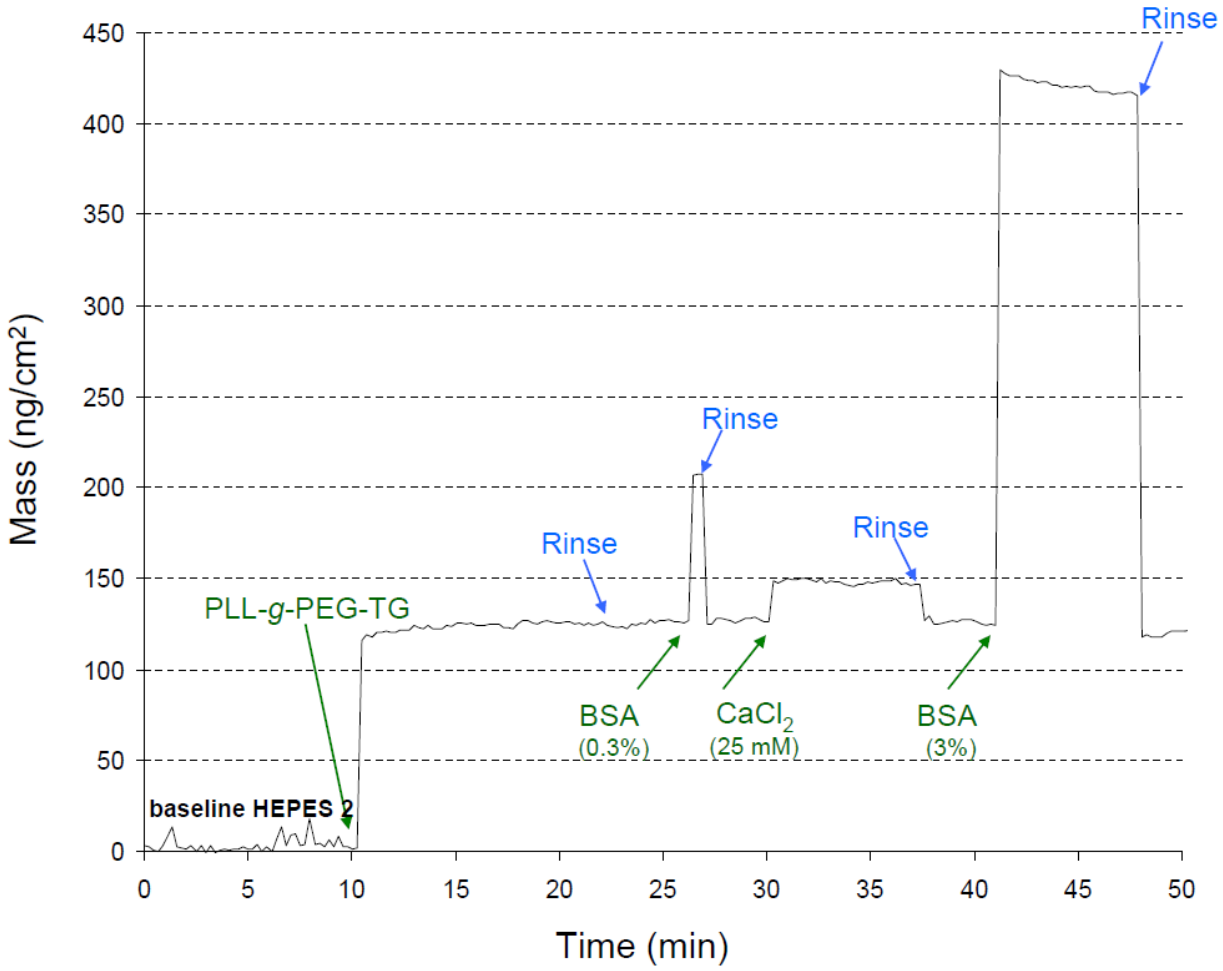


**Figure S2.** In situ OWLS PLL-*g*-PEG-TG adsorption and polymeric adlayer resistance to serum proteins (dn/dc = 0.139).

## 3. Summary of PLL-g-PEG-TG characterization by $^{1}$H-NMR and OWLS and theoretical peptide densities distance between them on the modified surfaces. Immobilization calculations on the surface.

**PLL-*g*-PEG-TG characterization by H-NMR and OWLS. Theoretical peptide densities based on these experimental values**

**PLL-*g*-PEG-TG characterization**

| Concept | | Remarks | Units | Values |
|---|---|---|---|---|
| Molecular weight PLL | *(mol wt PLL)* | | g/mol | 20.000 |
| N° Lys units | | | | 96 |
| Molecular weight Lys UNIT | *(mol wt Lys)* | | g/mol | 208,3 |
| Molecular weight PLL-*g*-PEG-TG | *(mol wt Pol)* | calculated (0) | g/mol | 78.513,7 |
| Molecular weight non-functionalized PEG side chains | | | g/mol | 2.000 |
| Molecular weight functionalized PEG side chains | | | g/mol | 3.400,0 |
| Molecular weight TG | | | g/mol | 1.358,5 |
| Grafting ration | *(g)* | experimental H-NMR | | 4,4 |
| Total number of PEG side chains | | experimental H-NMR | | 22 |
| Fraction of functionalized PEG | *($p_{PEG-TG}$)* | experimental H-NMR | % | 25% |
| Fraction of non-functionalized PEG | *($p_{PEG}$)* | experimental H-NMR | % | 75% |

***In situ* OWLS measurements**

| Concept | | Remarks | Units | Values |
|---|---|---|---|---|
| Mass of PLL-*g*-PEG-TG adsorbed on a $TiO_2$ waveguide | *($m_a$)* | (average of 5 independent experiments) | ng/cm$^2$ | 132 ± 5 |
| BSA adsorption (non-fouling properties of the PLL-*g*-PEG-TG adlayer) | | (average of 5 independent experiments) | ng/cm$^2$ | 1.8 ± 1.2 |
| Mass of PLL-*g*-PEG adsorbed on a $Nb_2O_5$ waveguide | *($m_a$)* | Not experimental. Reported value [15] | ng/cm$^2$ | 170 |

**Theoretical TG peptide density and distance between the moieties on a surface**

| Concept | | Remarks | Units | Values |
|---|---|---|---|---|
| TG peptide density on a $TiO_2$ surface | (ρ) | calculated (1) | pmol/cm$^2$ | 9,1 |
| Distance between the TG moieties on a $TiO_2$ surface | | calculated (2) | nm | 4,6 |
| TG peptide density on a $Nb_2O_5$ surface | (ρ) | calculated (1) | pmol/cm$^2$ | 11,7 |
| Distance between the TG moieties on a $Nb_2O_5$ surface | | calculated (2) | nm | 4,0 |

**Maximum theoretical peptide densities on a surface and Immobilization amounts.**

| Concept | Remarks | Units | Values |
|---|---|---|---|
| Molecular weight 8-arm Lys-PEG | | g/mol | 53.744,0 |
| Molecular weight Lys-FITC | | g/mol | 966,2 |
| Molecular weight Lys-RGD | | g/mol | 1.018,3 |
| Mass of 8-arm Lys-PEG immobilized on a $TiO_2$ surface (one-step). | calculated (3) | ng/cm$^2$ | 487,3 |
| Mass of Lys-FITC immobilized on a $TiO_2$ surface (one-step). | calculated (3) | ng/cm$^2$ | 8,8 |
| Mass of Lys-RGD immobilized on a $TiO_2$ surface | calculated (3) | ng/cm$^2$ | 9,2 |
| Mass of Lys-RGD immobilized on a $Nb_2O_5$ surface | calculated (3) | ng/cm$^2$ | 11,9 |

| | | | |
|---|---|---|---|
| Mass of 8-arm Lys-PEG immobilized on a $TiO_2$ surface (one-step). | calculated (3*) | ng/cm$^2$ | 39,0 |

| | | | |
|---|---|---|---|
| Molecular weight TG-VEGF | | | 32.000,0 |
| Molecular weight 8-arm TG-PEG | | | 50.868,0 |

| | | | |
|---|---|---|---|
| Mass of TG-VEGF immobilized on a $TiO_2$ surface (two-steps). | calculated (4); 1mol Lys-PEG to 1mol TG-VEGF | ng/cm$^2$ | 15.7 ± 2 |
| Mass of TG-VEGF immobilized on a $TiO_2$ surface (two-steps). | calculated (4*); 1mol Lys-PEG to 4mol TG-VEGF | ng/cm$^2$ | 62.9 ± 7.9 |
| Mass of TG-PEG immobilized on a $TiO_2$ surface (two-steps). | calculated (5); 1mol Lys-PEG to 1mol TG-PEG | ng/cm$^2$ | 25 ± 3.1 |
| Mass of TG-PEG immobilized on a $TiO_2$ surface (two-steps). | calculated (5*); 1mol Lys-PEG to 4mol TG-PEG | ng/cm$^2$ | 100 ± 12.5 |
| Mass of LYS-PEG immobilized on a $TiO_2$ surface (three-steps). | calculated (6); 1mol TG-PEG to 1mol Lys-PEG | ng/cm$^2$ | 25.6 ± 3.7 |
| Mass of LYS-PEG immobilized on a $TiO_2$ surface (three-steps). | calculated (6*); 1mol TG-PEG to 4mol Lys-PEG | ng/cm$^2$ | 102.3 ± 14.8 |

(0) [ mol wt (PLL) + [ [mol wt (PLL) / mol wt (Lys) * (1 / g)] * [((ρ$_{PEG}$ / 100) * mol wt (PEG)) + ((ρ$_{PEG-TG}$ / 100) * mol wt (PEG-TG))] ]

(1) [ [mol wt (PLL) / (mol wt (Lys) * g)] * [ (ma / mol wt (Pol)) * ρ$_{PEG-TG}$] ]

(2) [ [(2 / √3) * (1 / (ρ * Avogadro's number)]$^{1/2}$ ]

(3) [ ρ / mol wt (immobilized peptide via FXIIIa) ]; 100 % efficiency of the enzyme, all TG domains on the surface react with a Lys substrate

(3*) [ ρ / mol wt (immobilized peptide via FXIIIa) * 0.8 ]; 80 % efficiency of the enzyme, 1/10 TG domains on the surface react with a Lys substrate

(4) [ experimental 8-arm Lys-PEG immobilized (26.4 ± 3.3) / mol wt (8-arm Lys-PEG) * mol wt (TG-VEGF) ]

(4*) [ experimental 8-arm Lys-PEG immobilized (26.4 ± 3.3) / mol wt (8-arm Lys-PEG) * mol wt (TG-VEGF) ]

(5) [ experimental 8-arm Lys-PEG immobilized (26.4 ± 3.3) / mol wt (8-arm Lys-PEG) * mol wt (8-arm TG-PEG) ]

(5*) [ experimental 8-arm Lys-PEG immobilized (26.4 ± 3.3) / mol wt (8-arm Lys-PEG) * mol wt (8-arm TG-PEG) ]

(6) [ experimental 8-arm TG-PEG immobilized (24.2 ± 3.5) / mol wt (8-arm TG-PEG) * mol wt (8-arm Lys-PEG) ]

(6*) [ experimental 8-arm TG-PEG immobilized (24.2 ± 3.5) / mol wt (8-arm TG-PEG) * mol wt (8-arm Lys-PEG) ]

**Figure S3.** Summary of PLL-*g*-PEG-TG characterization by $^{1}$H-NMR and OWLS. Maximum theoretical peptide densities and distance between the TG moieties on the modified surfaces. Immobilization amounts (theoretical based on experimental values).

## 4. Representative OWLS experiment of enzymatic immobilization.

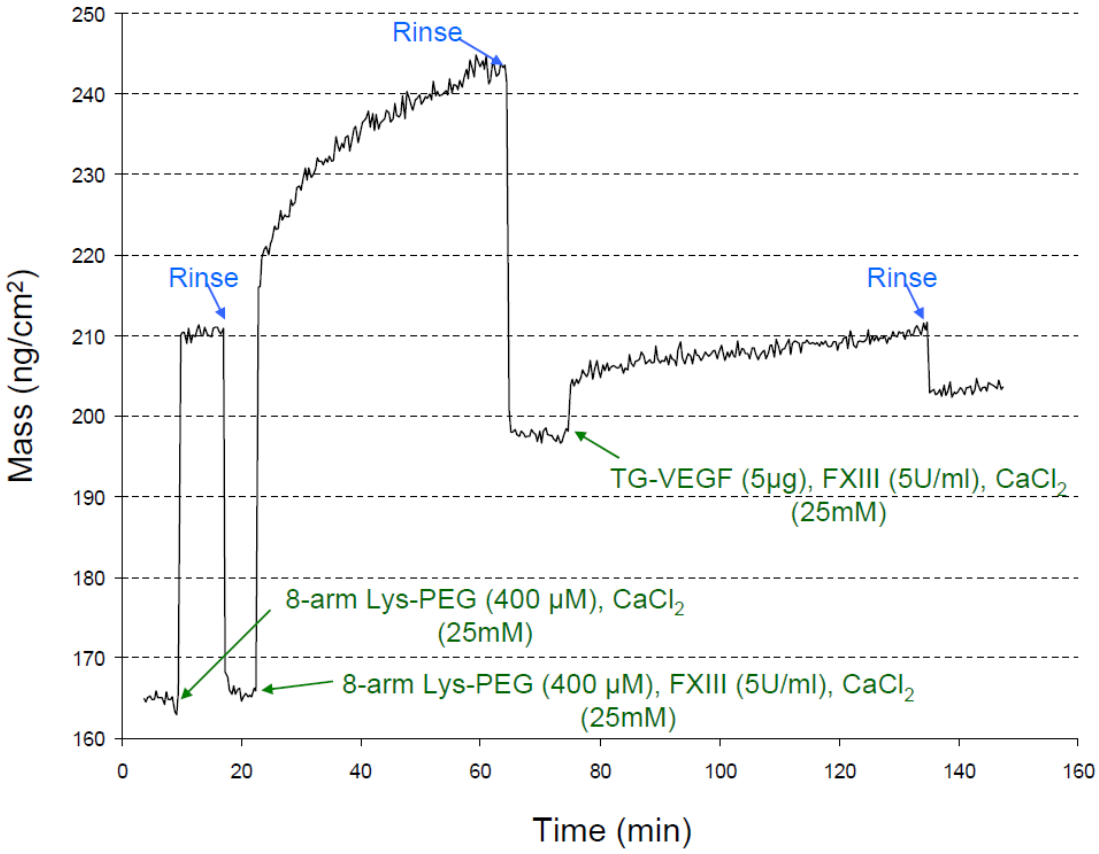


**Figure S4.** *In situ* OWLS immobilization of 8-arm Lys-PEG followed by TG-$VEGF_{121}$. First a negative control is shown (8-arm Lys-PEG in absence of FXIII). No absorption is observed. Next, immobilization of 8-arm Lys-PEG is monitored and followed by immobilization of TG-$VEGF_{121}$. The dn/dc for this graph is 0.139 (for PEG-based molecules. A dn/dc = 0.182 was considered for calculations involving TG-VEGF as mention in the Materials and Methods section). (Not real starting time).