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Supporting Information

Multifunctional REDV-Conjugated Zwitterionic Polycarboxybetaine-Polycaprolactone Hybrid Surfaces for Enhanced Antibacterial Activity, Hemocompatibility and Endothelial Cell Proliferation

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S1. Experimental Section

S1.1 Preparation of PCL films

The PCL films were prepared by a solution casting method. Typically, 5 g of PCL pellets was dissolved in 40 ml of methylene chloride to form the homogenous PCL solution. Subsequently, the PCL solution was cast onto a glass substrate with predetermined thickness using an film applicator. The solvent was then removed by slow evaporation under ambient pressure at room temperature over a period of 24 h, and was further dried in a vacuum oven at 35^{o}C for another 24 h. The as-prepared PCL films was translucent with a thickness of about 180 μm. Finally, the resultant PCL films were cut into round-shaped specimens with a diameter of 2 cm, and were used as the PCL scaffolds for the subsequent functionalization and multifunctionality tests.

S1.2 Aminolysis of PCL films

The activation of PCL films was achived by aminolysis treatment using a similar procedures described in detail previously. Briefly, the clean PCL films were introduced to a 10% (w/w) isopropanol solution of 1,6-hexanediamine at 40^{o}C for 30 and 60 min. After the animonlysis treatment, the PCL films were thoroughly rinsed with copious amount of isopropanol solution deionized water to remove free 1,6-hexanediamine, and dried in a vacuum oven at 30^{o}C for 24 h. The resultant aminolyzed PCL films for 30 and 60 min were defined as the PCL-NH_2-1 and PCL-NH_2-2 surfaces, respectively.

S1.3 Cultivation of *E. coli*

The *E. coli* strain used for the antibacterial assays were cultured in yeast-dextrose broth containing 10 g/L of peptone, 8 g/L of beef extract, 5 g/L of NaCl, 5

g/L of glucose, and 3 g of yeast extract at a pH of 6.8 at 37 ^{o}C for 36 h. After the cultivation, the bacteria-enriched broth was centrifuged at 2700 rpm for 10 min to harvest the *E. coli* bacterial cells. After the removal of the suspernant, the bacterial cells were washed twice with PBS and then resuspended in PBS at a concentration of 10^7 cells/mL. The bacterial cell concentration based on a standard calibration with the assumption that the optical density of 1.0 at 540 nm is equivalent to about 10^9 cells/mL. All the pristine PCL and surface-functionalized PCL films were sterilized with UV irradiation for 1 h prior to the experiment.

S1.4 Cell culture

Human umbilical vein endothelial cells (HUVECs, ATCC CRL-1730TM) were cultured in gelatin-coated T25 flasks containing MCDB131 cell culture medium supplemented with Foetal Bovine Serum, 0.2% Bovine Brain Extract, 0.25 ug/ml amphotericin, 0.1 mg/ml heparin, 100 U/ml penicillin, and 100 ug/ml streptomycin at 37 ^{o}C under conditions of 5% CO_2 atmosphere and 95% humidty. The HUVECs were subcultured upon reaching 80% confluency using 0.25% trypsin-EDTA (Gibco, Life Technologies) after washing twice with sterile PBS. Cells were provided with freshly prepared medium every 48 h and cells from passage 4-8 were used for the subsequent experiments.

S2. Results and Discussion

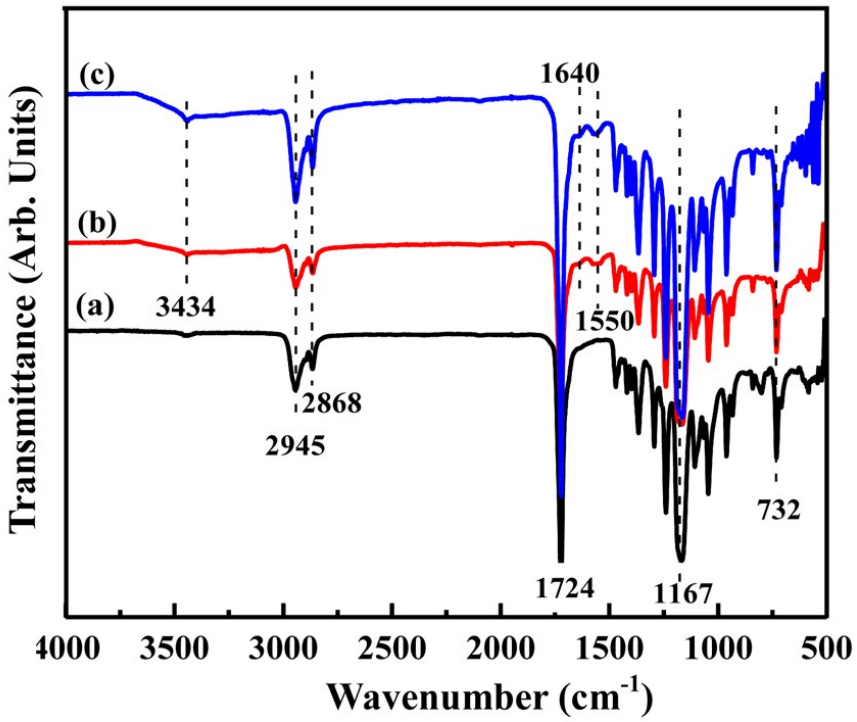

Fig. S1 ATR-FTIR spectra of the (a) pristine PCL, (b) PCL-NH_2-1 (from 30 min of aminolysis), and PCL-NH_2-2 (from 60 min of aminolysis). Successful introduction of amino groups onto the PCL substrates can be deduced from the appearance of characteristic bands at 3434 cm^{-1} ($\nu_{(N-H)}$), 1630 cm^{-1} (amide I) and 1536 cm^{-1} (amide II).

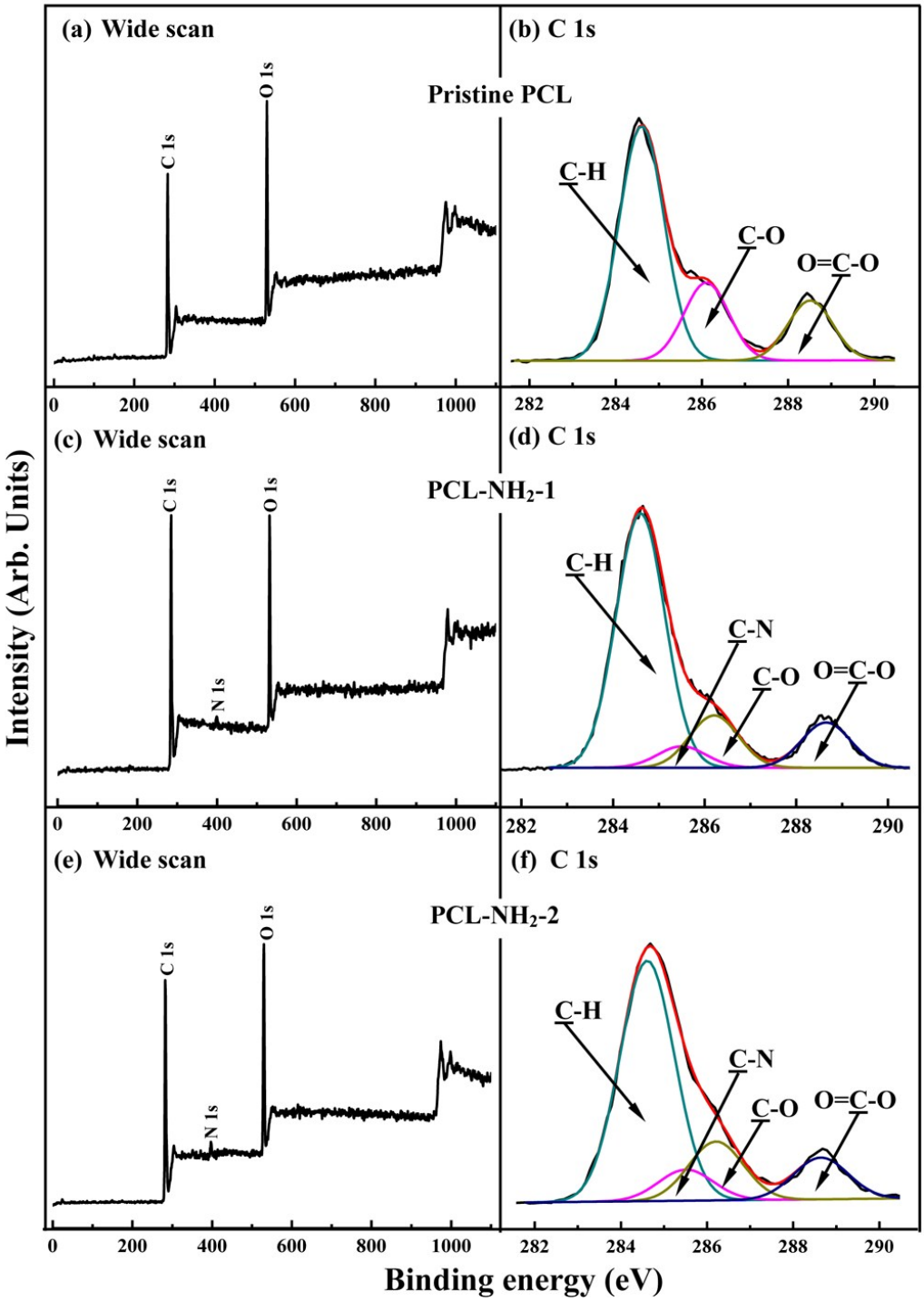

Fig. S2 Wide scan and C 1s core-level XPS spectra of the (a,b) pristine PCL, (c,d) PCL-NH_2-1 (from 30 min of aminolysis) and (e,f) PCL-NH_2-2 (from 60 min of aminolysis). The appearance of additional N 1s signals indicated the successful introduction of amino groups on the PCL substrates.

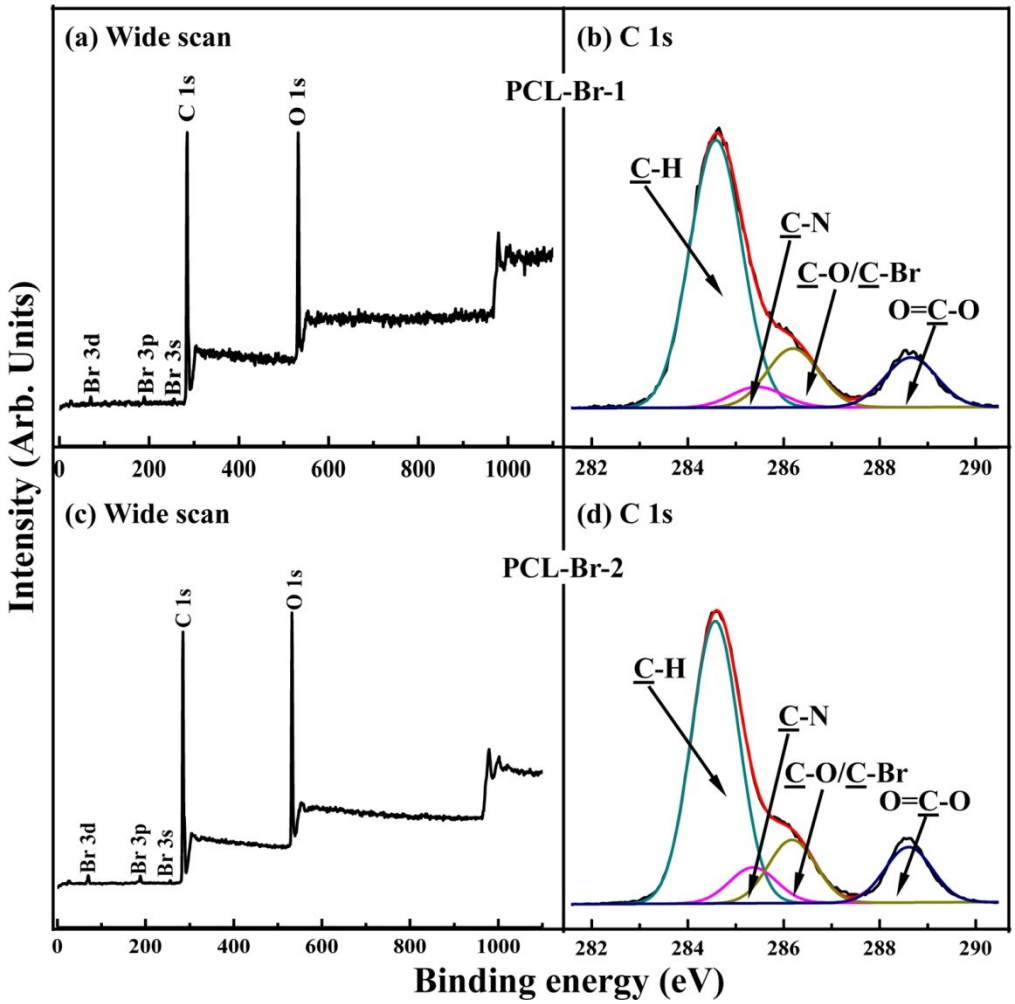

Fig. S3 Wide scan and C 1s core-level XPS spectra of the (a,b) PCL-Br-1 (from 30 min of aminolysis), (c,d) PCL-NH_2-1 (from PCL-NH_2-1 surface) and (e,f) PCL-NH_2-2 (from PCL-NH_2-2 surface). The appearance of additional N 1s signals indicated the successful introduction of amino groups on the PCL substrates.

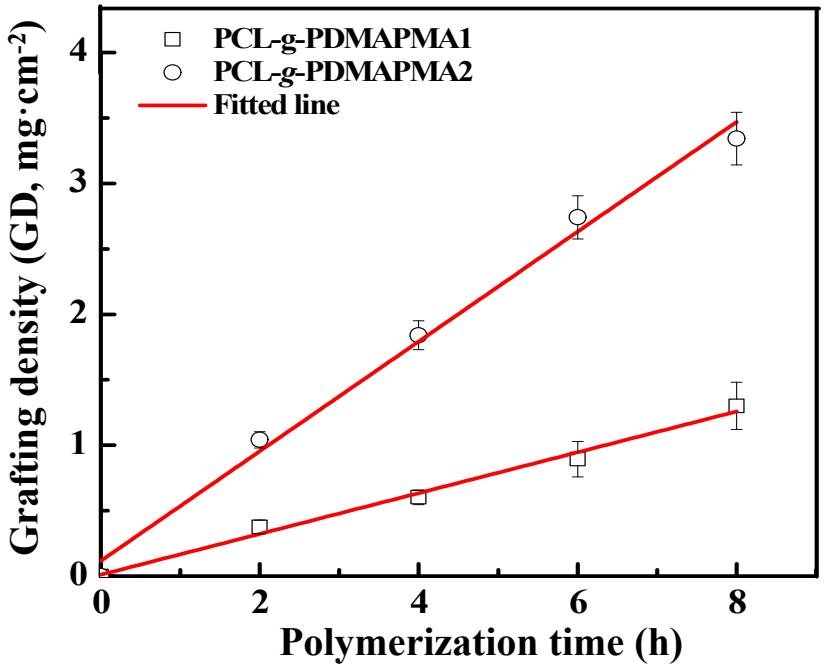

Fig. S4 A linear relationship for the grafting density of the PDMADMA brushes grafted from the respective PCL-Br-1 and PCL-Br-2 surfaces as a function of ATRP time. The PDMAPMA chain growth on the PCL substrates was found to proceed in a well-controlled manner by varying the surface density of ATRP initiator and reaction time.

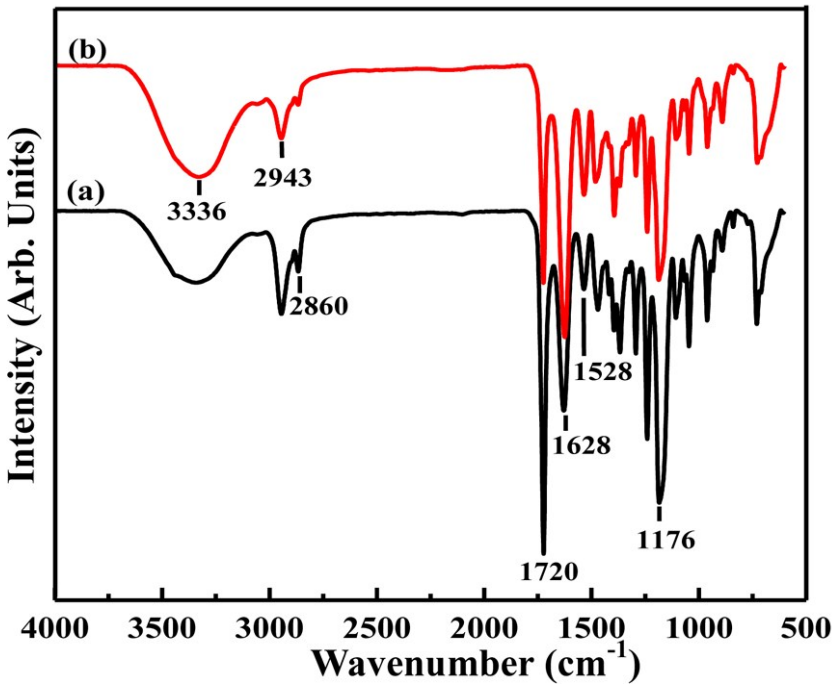

Fig. S5 FTIR spectra of the (a) PCL-g-QPDMAPMA1 (from the PCL-*g*-PDMAPMA1 surface), (b) CL-g-QPDMAPMA2 (from the PCL-*g*-PDMAPMA2 surface) surfaces. Successful *N*-alkylation of pendent tertiary amino groups of the PDMAPMA brushes was confirmed by the significant increase in the relative intensity of characteristic bands at 3336 cm^{-1} (ν_{O-H}), 1628 cm^{-1} (amide I, $\nu_{C=ONH}$) and 1528 cm^{-1} (amide II, δ_{N-H}).

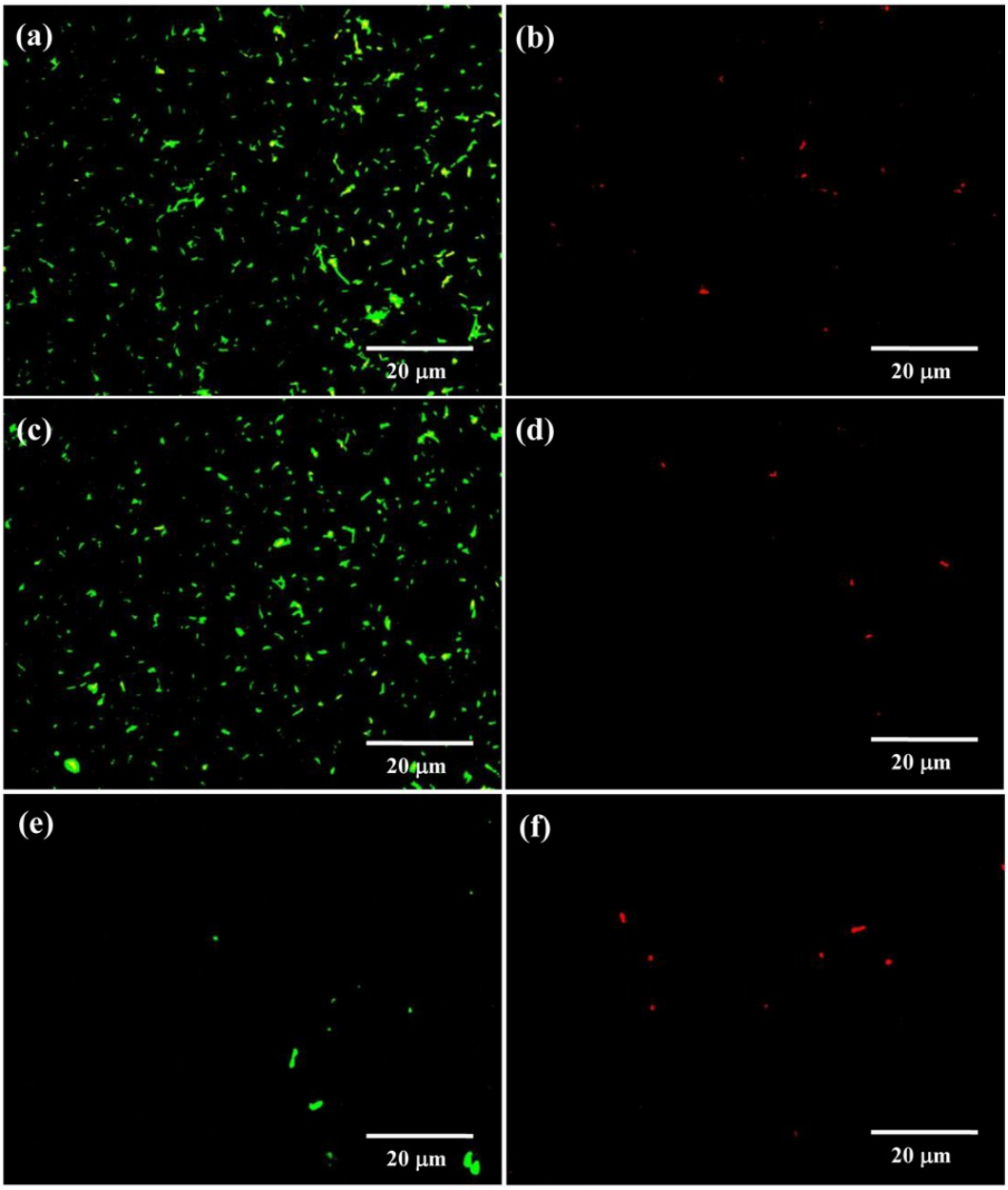

Fig. S6 Representative fluorescence microscopy images of *E. coli* attached on the (a,b) PCL-NH_2-2 (from 60 min of aminolysis), (c,d) PCL-*g*-PDMADMA2 (from the PCL-Br-2 surface) after 8 h of ATPR reaction, and (e,f) PCL-*g*-QPDAMPMA1 (from the PCL-g-PDMAPMA1 surface). The presence of zwitterionic Polycarboxybetaine brushes resulted in a significant reduction of *E. coli* amount attached to the PCL scaffold surface as compared to that on the aminolyzed and PDMAPMA-grafted surface.

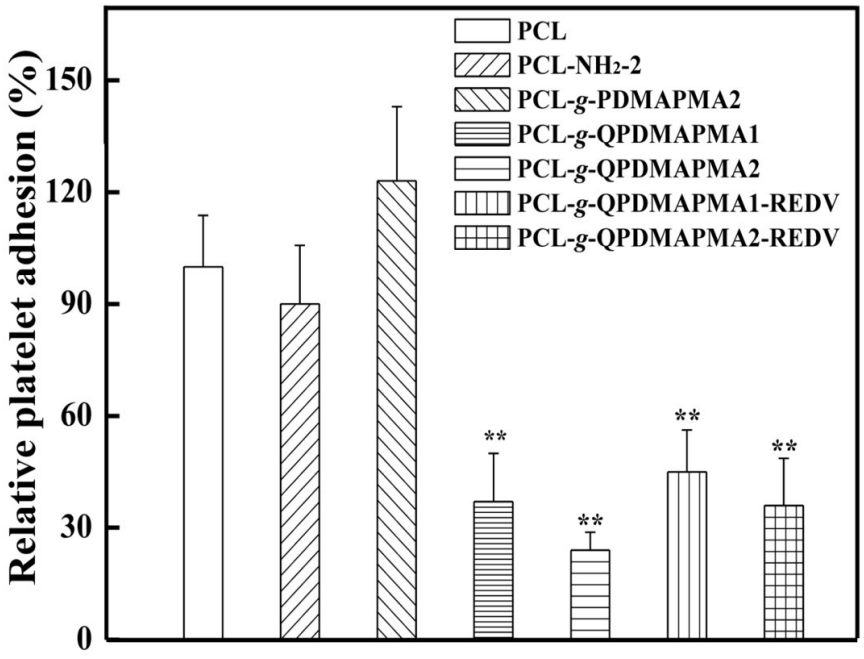

Fig. S7 Platelet adhesion results for the pristine PCL, PCL-NH_2-2, PCL-*g*-PDMAPMA2, PCL-*g*-QPDMAPMA2, PCL-*g*-QPDMAPMA2, (e) PCL-*g*-QPDMAPMA1-REDV, and PCL-*g*-QPDMAPMA2-REDV surfaces after 90 min incubation with platelet-rich plasma (PRP) at 37^{o}C.

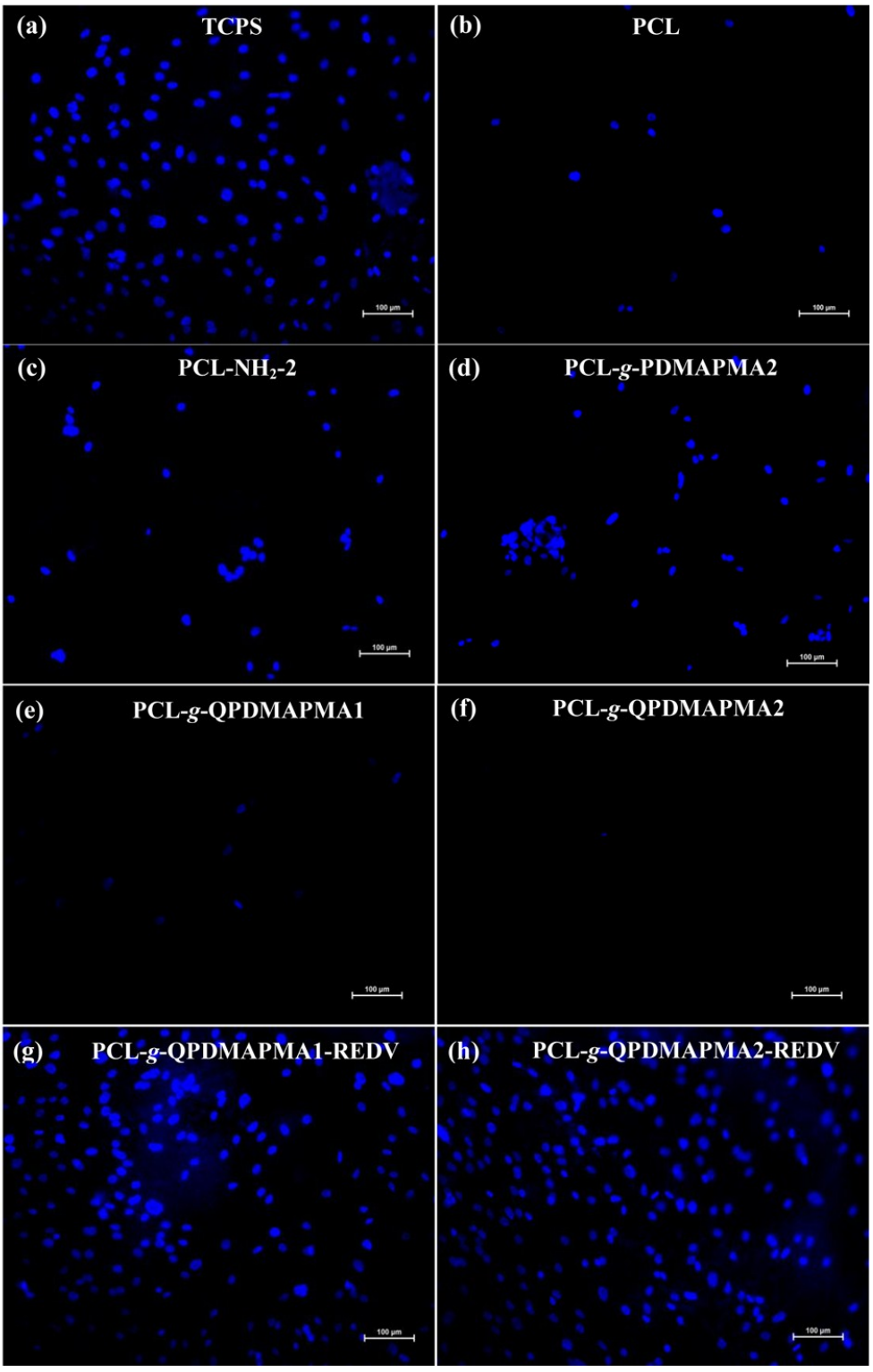

Fig. S8 Representative fluorescence images of DAPI-staining of ECs attached on the (a) TCPS control, (b) pristine PCL, (c) PCL-NH_2-2, (d) PCL-*g*-PDMAPMA2, (e) PCL-*g*-QPDMAPMA1, (f) PCL-*g*-QPDMAPMA2, (g) PCL-*g*-QPDMAPMA1-REDV

and (h) PCL-*g*-QPDMAPMA1-REDV surfaces after 24 h of incubation at 37^{o}C under a 5% CO_2 atmosphere. Scale bar: 100 μm. The substantial improvement in the attachment of ECs were observed on the conjugation of REDV peptide onto the PCL scoffold surfaces.