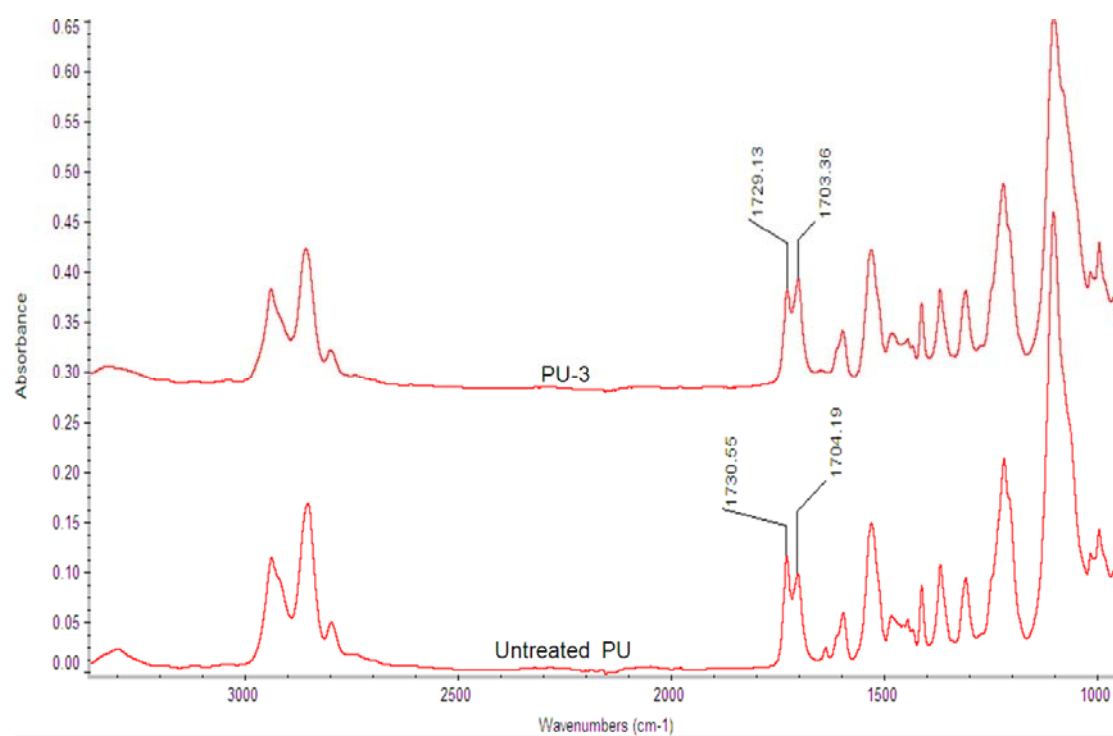
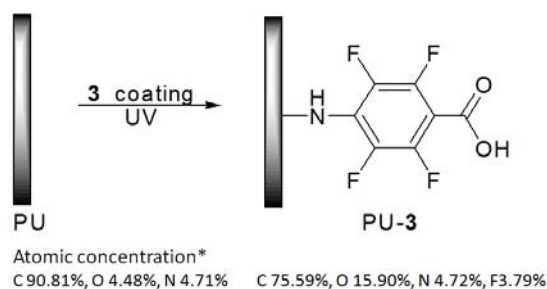


## Supporting information

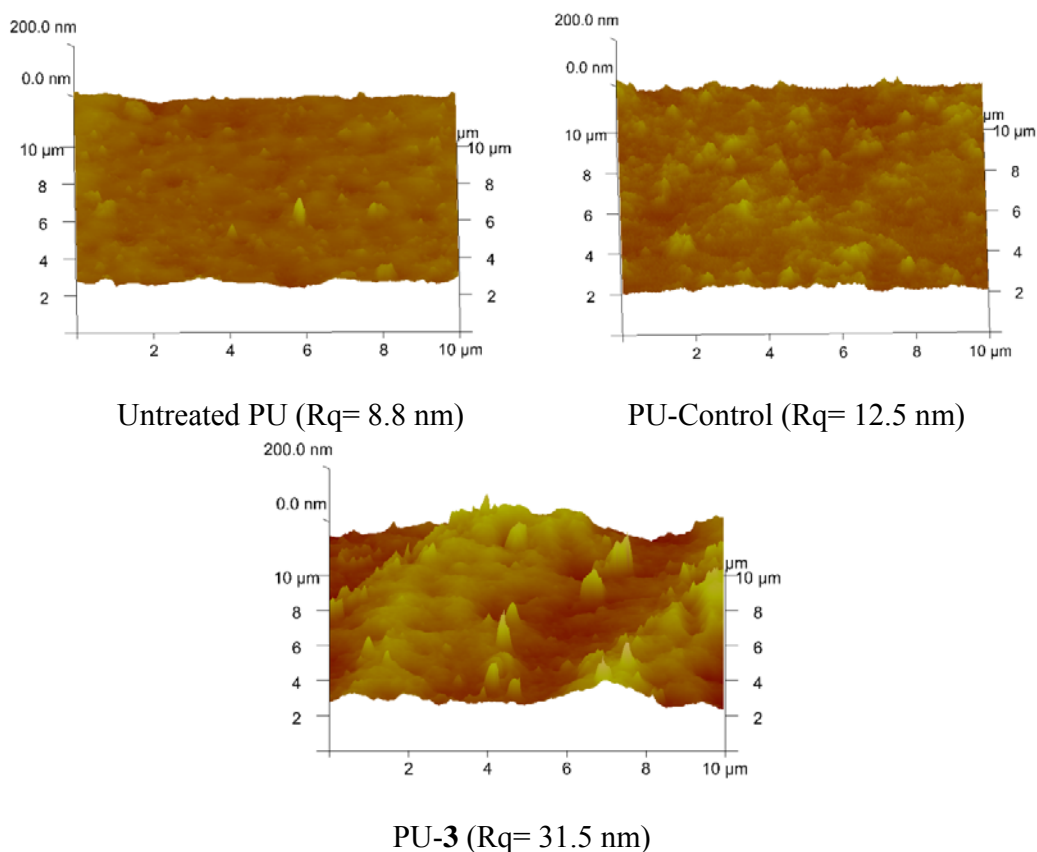


**Figure S1** ATR spectra of untreated PU and PU-3



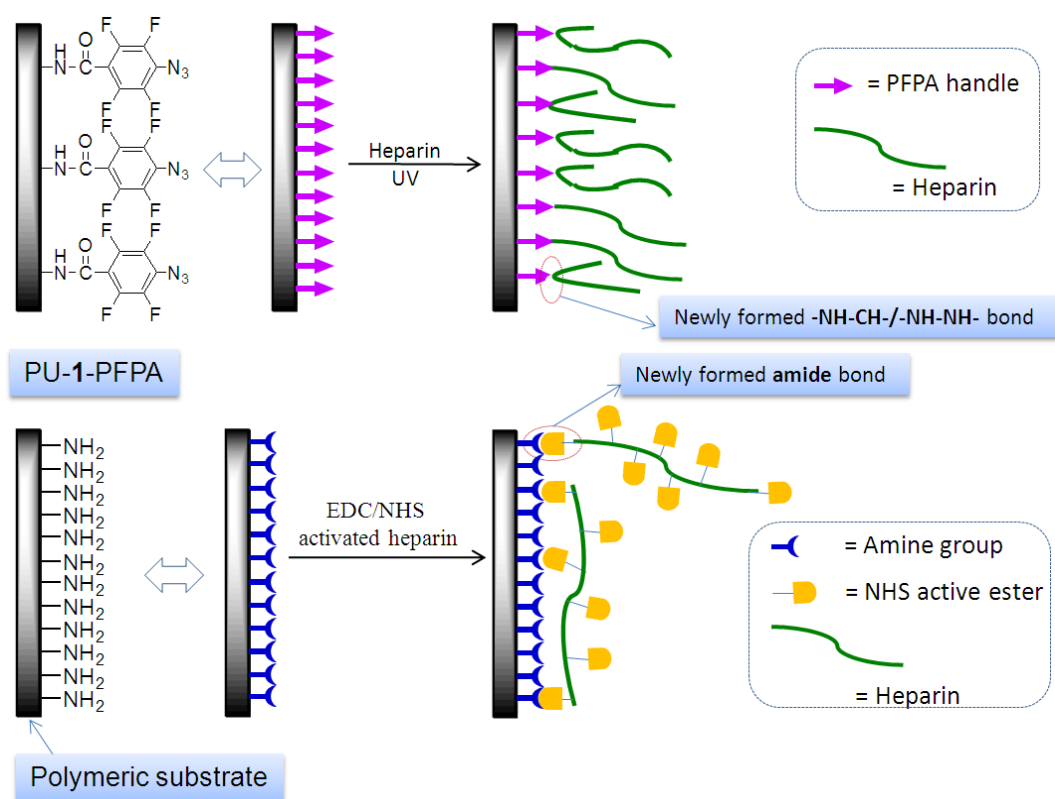
**Figure S2.** Calculation of surface functionalization level ( $\chi$ ) on PU-3.

\* Based on experimental XPS data analysis. Taking  $C_{38.56}O_{1.9}N_2$  ( $=C_{90.81}O_{4.48}N_{4.71}$ ) as the formula for a repeating unit, the C/F of PU-3 could be calculated as:  $(38.56+7\chi)/4\chi = 75.59\%/3.79\% = 19.94$  since the formula of **3** is  $C_7HO_3N_3F_4$ . Thus far,  $\chi = 53.0\%$  is obtained.

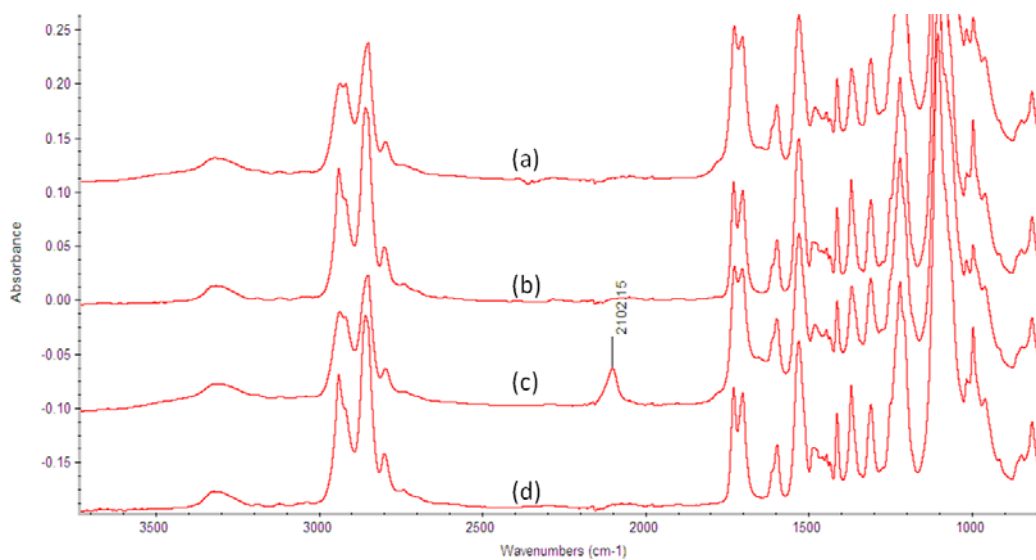


**Figure S3.** AFM spectra of untreated PU, PU-Control (PU film which had gone through the similar treatment as PU-3 except without the presence of **3**), and PU-3.

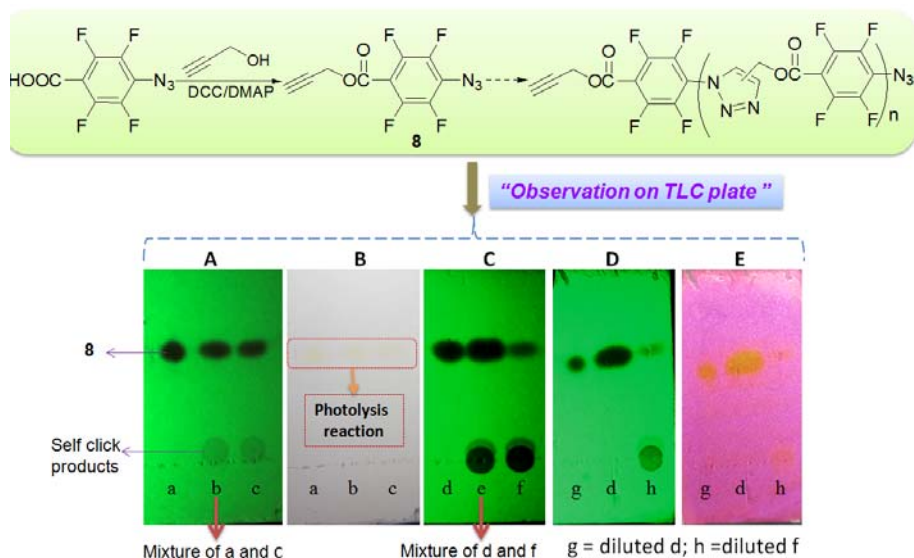
$R_q$  is the root mean square roughness.



**Figure S4.** Proposed bonding manner of heparin immobilized via PFPF photo-coupling chemistry and carbodiimide chemistry.

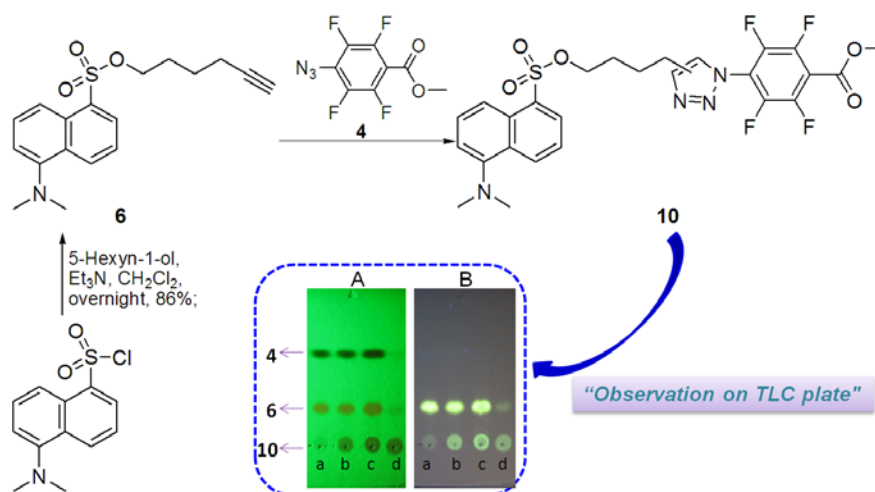


**Figure S5.** ATR spectra of (a) untreated PU; (b) PU-1; (c) PU-1-azide; (d) PU-1-azide (back side).



**Scheme S6.** Synthesis of **8** and the self-click observation on TLC plate. A, C and D were observed under 254 nm while B and D under daylight (E sprayed with 0.5%  $\text{KMnO}_4$ ); A/B and D/E are the identical plate respectively; the developing solvent is EtOAc/Hex = 1:10; Synthesis of **8** was readily completed using DCC as coupling agent. After column chromatography, the eluted fraction containing **8** (Figure S6 A/B-a) was checked by TLC to present a single spot. After being concentrated on rotary evaporator (water bath  $37^\circ\text{C}$ , ca. 20 min), a new more polar spot appeared close to the baseline (S6 A-c). After UV irradiation, slight yellowish spots could be seen as shown in Figure S6 B, indicating that the PFPA moieties in **8** underwent the photolysis reaction. Sample a was stored at  $4^\circ\text{C}$  for 40 h (weekend) to find that it remained intact (Figure S6 D-d). Meanwhile, an aliquot sample a was also stored in an open vial at RT to spontaneously evaporate the solvent. After 40 h, TLC analysis of the obtained white solid showed that the majority of **8** converted to a new compound as depicted in Figure S6 D-f. It seemed that the concentration of eluted fraction containing **8**, namely, the possibility of conflict between the molecules, accounted for its stability. After being sprayed with 0.5%  $\text{KMnO}_4$  solution, a yellow spot appeared as shown in Figure S6 E-d/g (sample g is diluted sample d) indicating that the alkyne moiety in **8** was oxidized by  $\text{KMnO}_4$ . However, for the newly formed spot (Figure S6 E-h, h is diluted f), the yellowish color was barely observed. Comparing g and h in Figure S6 D/E, it could be inferred that the majority of alkyne groups probably were involved in the click reaction to give the triazole moieties that were insensitive to 0.5%  $\text{KMnO}_4$  solution.

In principle, self-click of **8** could lead to a mixture of polymers with different molecular weights and therefore the alkyne content decreased after UV irradiation.



**Figure S7.** Synthesis of dansyl-alkyne **6** and self-click reaction with **4**. A: observation under 254 nm and B: observation under 365 nm. Model reaction between **6** and **4** was performed as follows: 100  $\mu\text{L}$  solution **6** (0.15 mol/L in ethyl acetate) and 100  $\mu\text{L}$  solution **4** (0.15 mol/L in ethyl acetate) were mixed well in a 1.5 mL centrifuge tube. The mixture was left stand at RT and 37°C respectively, with the tube open overnight to evaporate the solvent spontaneously. The residue (a, RT; b, 37°C) was then checked by TLC analysis. Meanwhile, 100  $\mu\text{L}$  solution and 105  $\mu\text{L}$  solution was also mixed well in presence of 40% Na ascorbate and 10%  $\text{CuSO}_4$  (dissolved in 200  $\mu\text{L}$  water and 200  $\mu\text{L}$  acetone). The mixture was shaken continuously for 2 h and subsequently concentrated, followed by the addition of 0.5 mL ethyl acetate. The resultant organic solution (d) was also checked on TLC plate as depicted in Figure S-7 A/B; Sample c is the mixture of a, b and d.