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 $C_7H_5O_3N_3F_4$. 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. Rq 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% KMnO₄); 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°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°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% KMnO₄ 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 KMnO₄. 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% KMnO₄ 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 µL solution 6 (0.15 mol/L in ethyl acetate) and 100 µL 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 µL solution and 105 µL solution was also mixed well in presence of 40% Na ascorbate and 10% CuSO₄ (dissolved in 200 µL water and 200 µL 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.