Electronic Supplementary Information

Multifaceted and Route-Controlled "Click" Reactions Based on Vapor-Deposited Coatings

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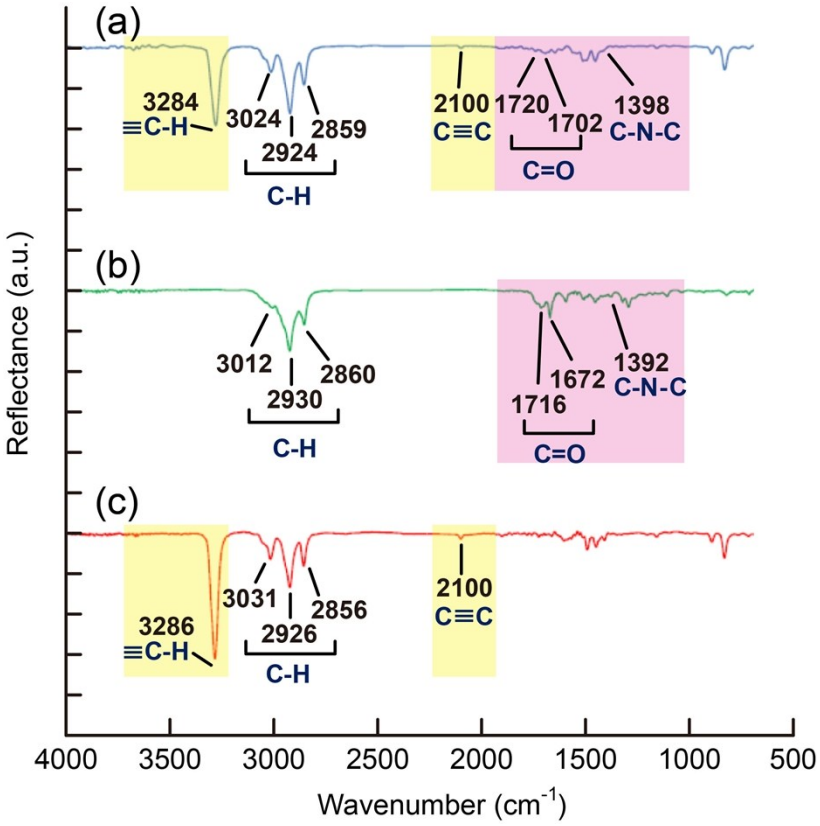

Fig. S1 IRRAS spectra comparing the (a) double-clickable PPX with monosubstituted (b) poly[(4-N-maleimidomethyl-*p*-xylylene)-*co*-(*p*-xylylene)] and (c) poly[(4-ethynyl-*p*-xylylene)-*co*-(*p*-xylylene)]) (route-clickable PPX). The characteristic bands of the monosubstituted coatings from (b) and (c) were also detected in double-clickable PPX, indicating that both the ethynyl and maleimide groups were preserved during the CVD copolymerization process. The polymer coatings were prepared on gold substrates for the IRRAS characterizations.

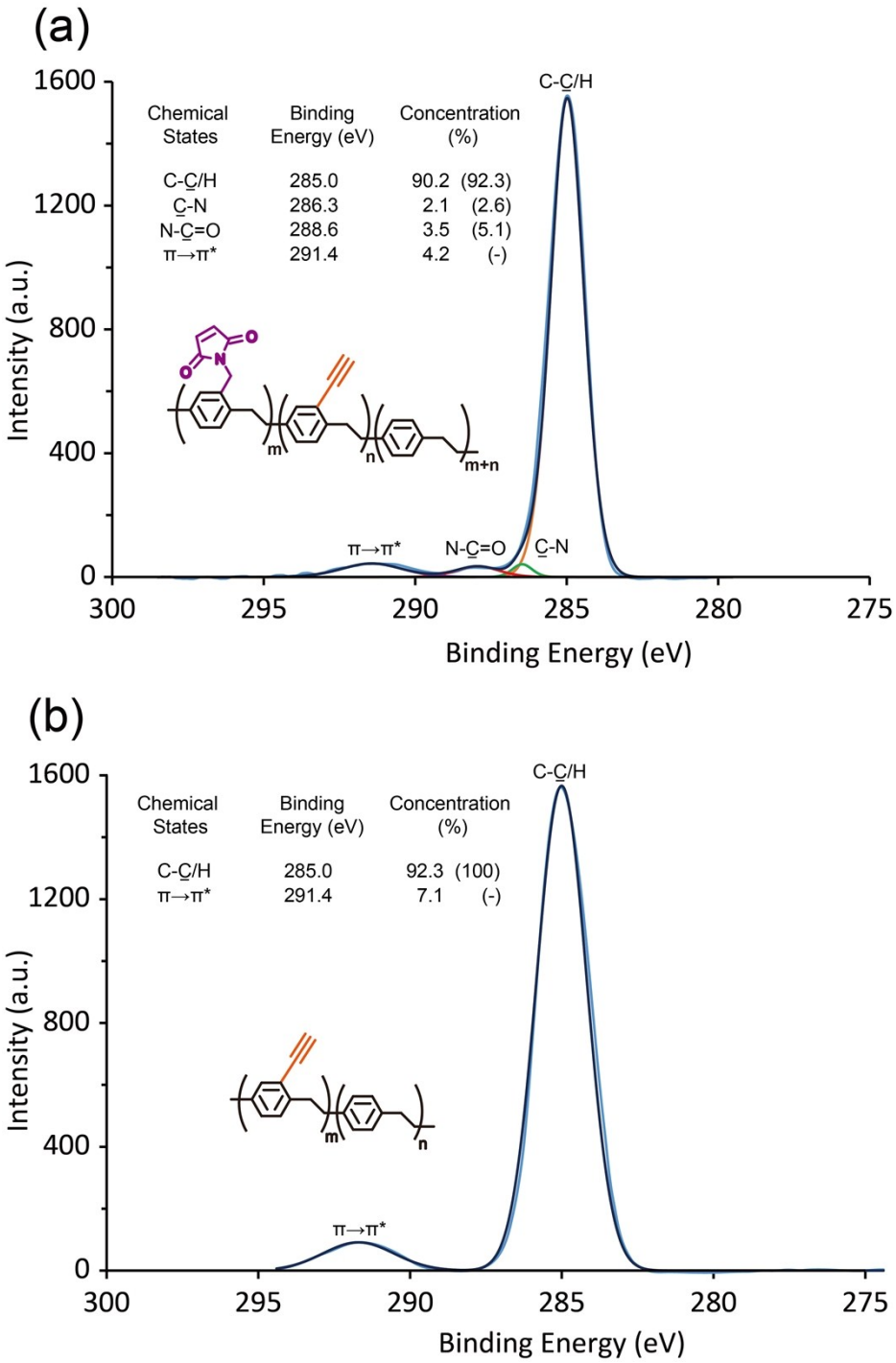

Fig. S2 XPS high-resolution C_{1s} spectra of (a) double-clickable PPX and (b) route-clickable PPX. Experimental values are found consistent with calculated values (in the bracket). The data for double-clickable PPX were analyzed based on an equimolar distribution of starting materials. The polymer coatings were prepared on silicon substrates for the XPS characterizations.

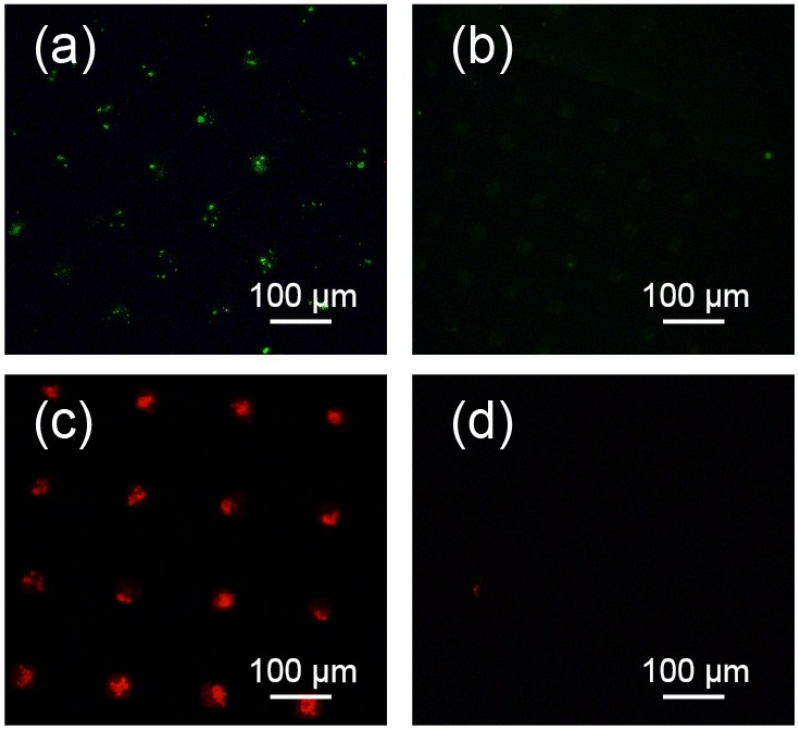

Fig. S3 Verification of cross-reaction for monodistributed ethynyl or maleimide functionalized surface. (a) Fluorescent image displaying absorbed fluorescein-labeled cysteines on the poly[(4-ethynyl-*p*-xylylene)-*co*-(*p*-xylylene)] coating after using a μCP process for 2 h at room temperature. The image was recorded prior to washing. (b) Fluorescent image of the sample (a) after washing. (c) Fluorescent image revealing the absorbed Alexa Fluor 555 azides on the poly[(4-*N*-maleimidomethyl-*p*-xylylene)-*co*-(*p*-xylylene)] coating after using a μCP process for 2 h at room temperature. The image was recorded prior to washing. (d) Fluorescent image of the sample (c) after washing. The polymer coatings were prepared on gold substrates for the study.

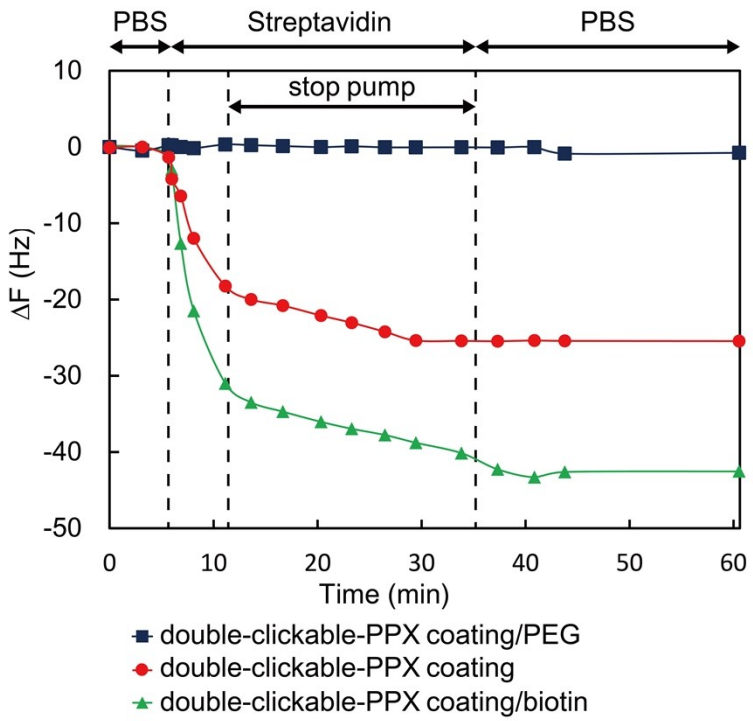

Fig. S4 QCM analysis of the antifouling and biotinylated activities on double-clickable PPX. Noticeable adsorption of streptavidin was observed on pure double-clickable PPX (an average frequency/adsorption of 25.5 Hz/139.0 ng cm^{-2}). After modifying the PEG groups on double-clickable PPX, the non-specific streptavidin adsorption was dramatically reduced (an average frequency/adsorption of 0.8 Hz/4.2 ng cm^{-2}). Finally, by attaching both PEGs and biotins to double-clickable PPX, the surface utilizes a synergistic approach that suppresses the non-specific binding of streptavidin and precisely induces controlled binding through a biotin/streptavidin interaction (an average frequency/adsorption of 42.5 Hz/232.2 ng cm^{-2}).

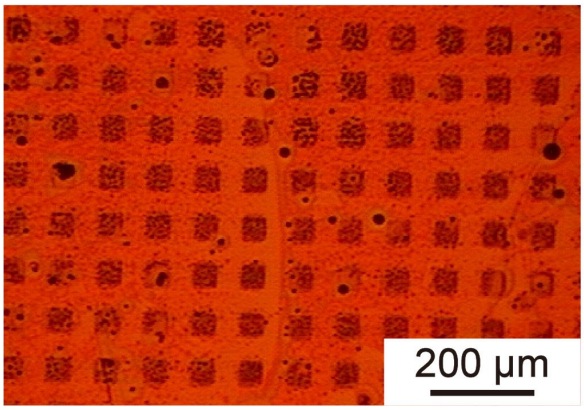

Fig. S5 Phase contrast image showing selectively adsorbed water molecules on the hydrophilic regions (dark regions) that have been modified with thiol-PEGs via the thiol-yne click reaction compared to the poor water absorption on the hydrophobic polymer regions on the background (reddish regions) where thiol-PEG modification was absent. A route-clickable PPX (poly(4-vinyl-*p*-xylylene-*co*-*p*-xylylene))-coated gold substrate was used as a model substrate, and thiol-PEGs were coupled through a photochemical thiol-yne click reaction.

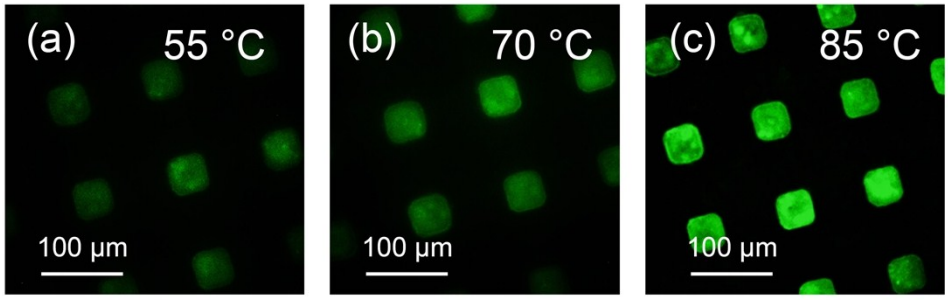

Fig. S6 Fluorescein-labeled RGDYCC peptide was immobilized on route-clickable PPX via the thermally activated thiol-yne reaction under various thermal conditions in (a) 55 °C, (b) 70 °C, and (c) 85 °C. The reactions were confined to selected areas using a µCP process with 50 µm x 50 µm array patterns. The polymer coatings were prepared on gold substrates for the study.

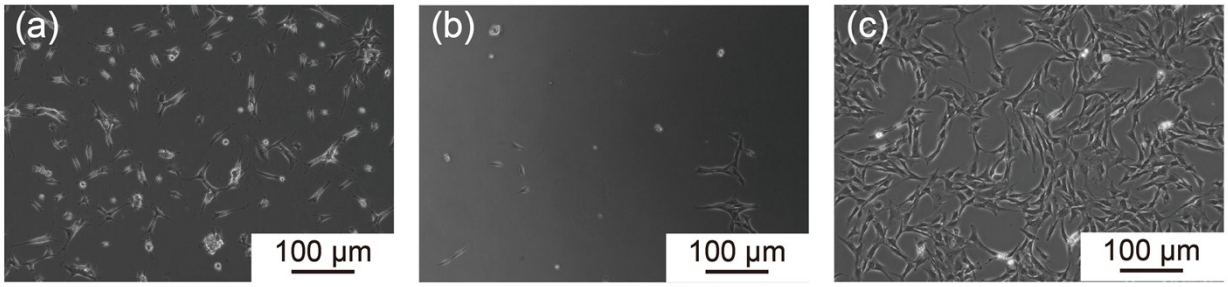

Fig. S7 Control experiments for 3T3 fibroblast cells cultured on route-clickable PPX modified substrates. (a) Mild adhesion and growth of 3T3 occurred on the pure route-clickable PPX surface. (b) No 3T3 cells attached to the surface after immobilizing PEGs on route-clickable PPX. (c) Populated growth of 3T3 was observed after immobilizing RGDYCC peptides on route-clickable PPX. The observations were recorded after a 24 h incubation period. Immobilizations of thiol-PEG and RGDYCC were performed via the photochemical thiol-yne reaction on route-clickable PPX. The polymer coatings were prepared on tissue culture polystyrene (TCPS) microplates for the study.