

Supporting Information

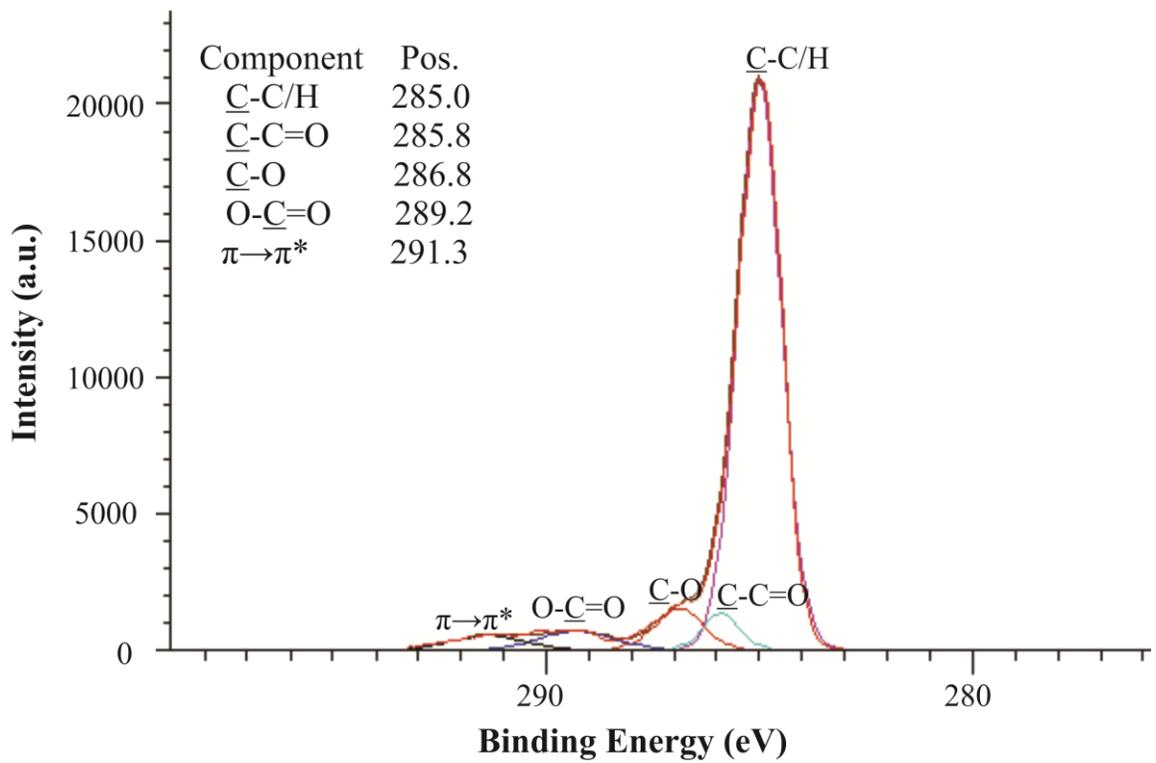
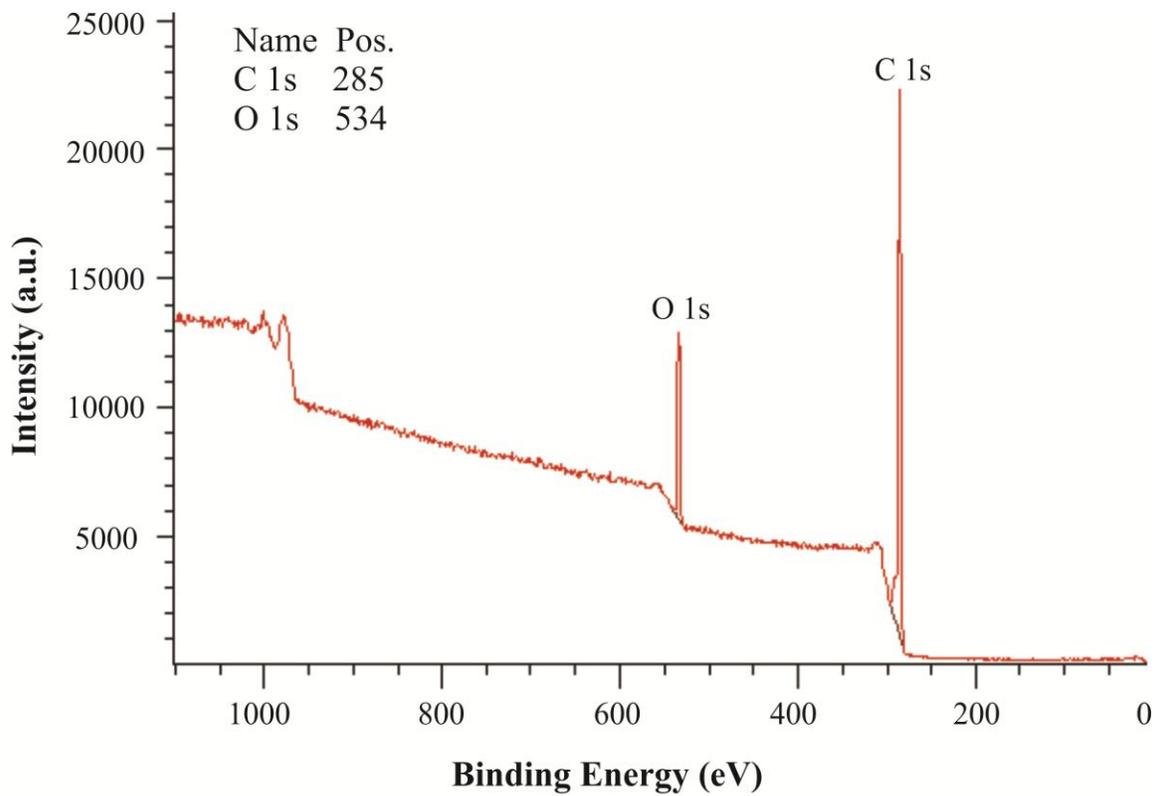
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Bio-orthogonal “Double-Click” Chemistry Based on Multifunctional Coatings

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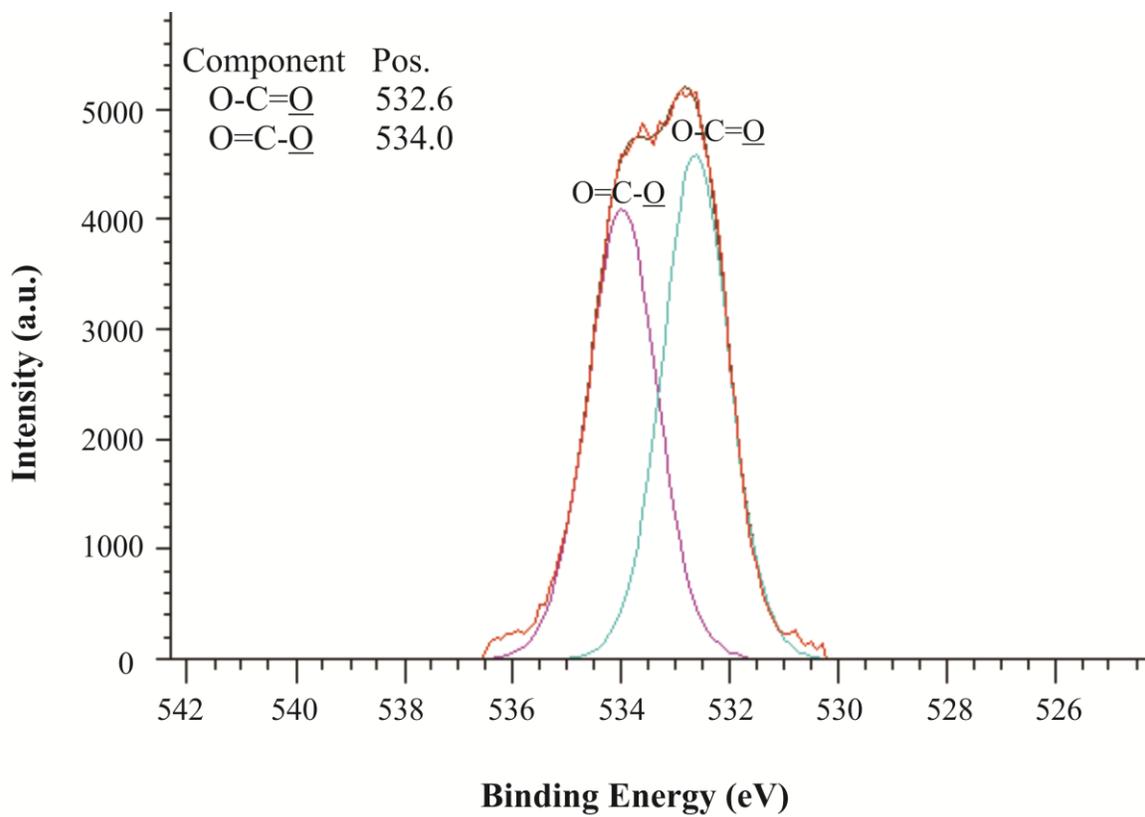


Figure S1. XPS survey spectrum and high resolution peak fittings corresponding to the reported in the table of Figure 1.

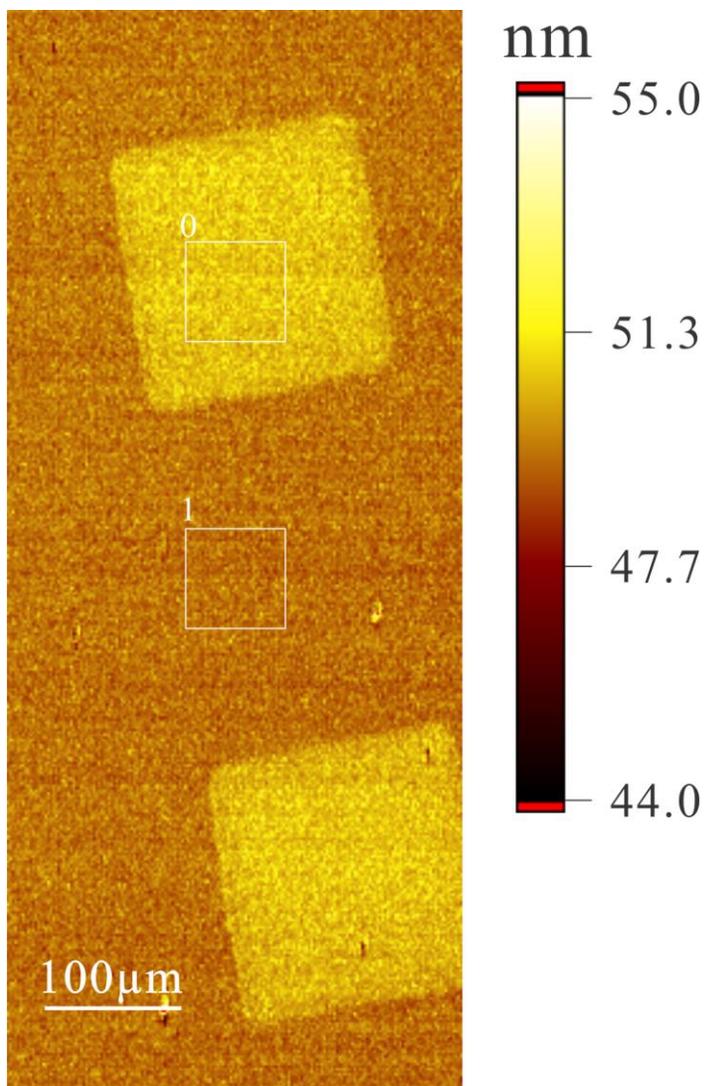


Figure S2. Thickness measurement on the micro-engineered surface by Imaging Ellipsometry. The thickness map was generated from delta map at 658nm by modeling. For more accurate measurement, multiwavelength 4-zone nulling was used to measure the average thickness of the region of interest (ROI) 0 and 1 in the image. For this particular sample, thickness for ROI 0 and ROI 1 is 51.2 nm and 48.1 nm respectively.

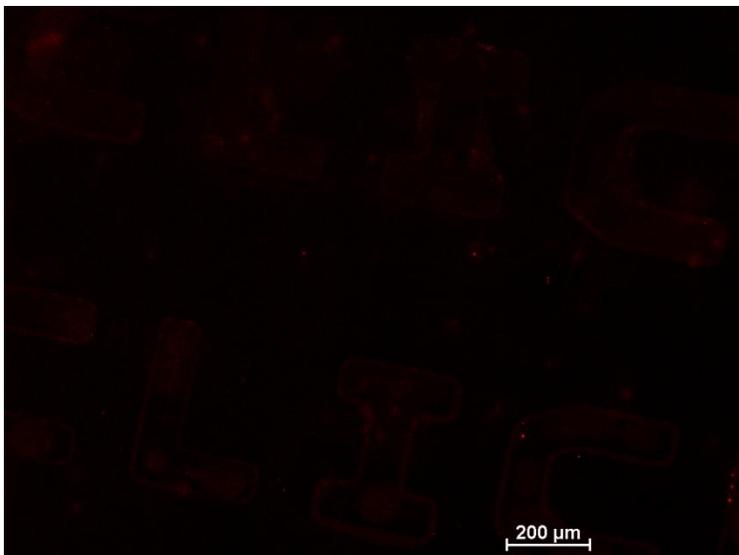


Figure S3. Fluorescence image for 10 seconds printing on polymer 2.

Experimental Section

Synthesis of precursors for CVD polymerization

General:

All chemicals were purchased from Aldrich and VWR and used without further purification. Routine monitoring of reactions was performed using Silica gel coated alumina plates (silica gel 60), which were analyzed under UV-light at 254 nm. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance III spectrometer as solutions. Mass spectra were recorded on a Finnigan MAT95. IR spectra were recorded on a Bruker Alpha T using ATR (attenuated total reflectance) sampling technique. Melting points were measured on a Stanford Research Systems Optimelt.

The synthesis of 4-ethynyl[2.2]paracyclophane was described elsewhere.^[1]

[2.2]Paracyclophane-4-methyl propiolate was synthesized from previously published 4-hydroxymethyl[2.2]paracyclophane.^[2] 4-Hydroxymethyl[2.2]paracyclophane (2.53 g, 10.6 mmol) and 4-dimethylaminopyridine (13.0 mg, 0.11 mmol) were dissolved in dichloromethane (60 mL). Propiolic acid (724 μ L, 820 mg, 11.7 mmol) was added and the solution was cooled to 0 °C. Then *N,N'*-diisopropylcarbodiimide (1.82 mL, 1.48 g, 11.6 mmol) was added dropwise over 10 minutes and the mixture was warmed to room temperature and stirred for another 6 hours. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent: dichloromethane/hexane 2:1). [2.2]Paracyclophane-4-methyl propiolate (2.38g, 77%) was obtained as a white solid.

¹H NMR (500 MHz, CDCl₃): 6.60 (dd, *J* = 7.9 Hz, 1.8 Hz, 1H, CH), 6.57–6.48 (m, 4H, CH), 6.41–6.38 (m, 2H, CH), 5.18 (d, *J* = 12.4 Hz, 1H, CH₂O), 4.99 (d, *J* = 12.4 Hz, 1H, CH₂O), 3.35 (ddd, *J* = 13.5 Hz, 10.2 Hz, 2.3 Hz, 1H, CH₂), 3.17 (ddd, *J* = 13.4 Hz, 11.0 Hz, 2.4 Hz, 1H, CH₂), 3.14–2.97 (m, 5H, CH₂), 2.92 (ddd, *J* = 13.7 Hz, 10.8 Hz, 5.8 Hz, 1H, CH₂), 2.88 (s, 1H, CH)

ppm. ^{13}C NMR (125 MHz, CDCl_3): 152.7, 140.3, 139.6, 139.1, 138.5, 135.2, 134.1, 133.4, 133.3, 133.2, 132.9, 132.2, 129.7, 75.0, 74.6, 67.0, 35.2, 34.9, 34.5, 32.9 ppm.

EI-MS [70 eV, m/z (%): 290 (9) [M^+], 220 (14) [$\text{C}_{17}\text{H}_{16}^+$], 132 (36) [$\text{C}_9\text{H}_8\text{O}^+$], 104 (100) [C_8H_8^+], 77 (38) [C_6H_5^+]. HR-MS (EI): 290.1307 (calculated for [M^+], $\text{C}_{20}\text{H}_{18}\text{O}_2$), 290.1304 (observed).

FT-IR (ATR): 3259 (vw), 2923 (vw), 2850 (vw), 2116 (vw), 1696 (w), 1497 (vw), 1461 (vw), 1435 (vw), 1413 (vw), 1377 (vw), 1250 (w), 1221 (m), 953 (w), 903 (w), 873 (vw), 797 (w), 753 (w), 716 (w), 643 (w), 616 (vw), 578 (w), 512 (w), 479 (vw), 410 (vw) cm^{-1} .

m.p.: 145 °C.

CVD polymerization

Poly[(4-ethynyl-*p*-xylylene)-co-(*p*-xylylene)] (**1**) and poly[(*p*-xylylene-4-methyl-propiolate)-co-(*p*-xylylene)] (**2**) were synthesized via CVD polymerization as shown in Scheme 1. The CVD process was carried out at 0.3 mbar, with 20 sccm argon as carrier gas. The precursor was sublimed at 90-110°C in vacuum and converted into corresponding diradical by pyrolysis (>500°C). The diradicals spontaneously polymerized on the cooled (15°C) substrate placed on top of a rotating stage. The pyrolysis temperature was set to be 670 °C for polymer 1 and 510 °C for polymer 2. The resulted film thickness was around 50 nm for all the experiments. To generate micro-engineered surface by 2-step CVD as shown in Figure 4, polymer **1** was first coated on the whole surface, followed by polymer **2** coated on selected areas of the surface with the help of PDMS microstencil. The fabrication of PDMS microstencil was described in our previous papers.^[2-3]

Surface Characterization:

IR spectra were recorded on a Nicolet 6700 spectrometer with the grazing angle accessory (Smart SAGA) at a grazing angle of 85°. XPS were performed on an Axis Ultra X-ray photoelectron

spectrometer (Kratos Analyticals, UK) equipped with a monochromatized AlK α X-ray source. All spectra were calibrated with respect to the non-functionalized aliphatic carbon with a binding energy of 285.0 eV. Thicknesses were measured on silicon substrate by Imaging Spectroscopic Ellipsometer (Accurion, Nanofilm EP 3 SE). Ellipsometric parameters were fitted using Cauchy model. Both multi-wavelength 4-zone nulling and mapping experiments were performed at an angle of incidence of 70°. The imaging lateral resolution is ~2 micron for the 10 \times objective.

Surface Immobilization

For microcontact printing, PDMS stamps were inked with water solution of Biotin-dPEG $^{\text{®}$ ₃₊₄-azide (10mg/ml, Quanta BioDesign, Ltd.) and printed for 3 h on different polymer surfaces. After thorough washing, the samples were incubated in TRITC conjugated streptavidin (10 μ g/ml, Fisher Scientific) in PBS containing 0.1 % (w/v) bovine albumin and Tween 20 (0.02 % (v/v)) for 1 h. Subsequently, the samples were washed, dried and observed under fluorescence microscope (Nikon Eclipse 80i).

Similarly, for solution reactions on microengineered surfaces, samples were incubated in solution of Biotin-dPEG $^{\text{®}$ ₃₊₄-azide (10mg/ml, without copper for Figure 3 and with copper for Figure 4) for 12h followed by washing and TRITC-streptavidin incubation described above. For the experiment in Figure 4, the sample was first incubated in copper-free water solution of Oregon Green $^{\text{®}$ 488 azide (20 μ g/ml, Invitrogen) for 12h. Subsequently, the sample was washed and incubated in Biotin-dPEG $^{\text{®}$ ₃₊₄-azide solution with sodium ascorbate (50mg/ml) and copper sulfate (0.1mM).

- [1] H. Nandivada, H. Y. Chen, L. Bondarenko, J. Lahann, *Angew Chem Int Edit* **2006**, *45*, 3360-3363.
- [2] X. W. Jiang, H. Y. Chen, G. Galvan, M. Yoshida, J. Lahann, *Adv Funct Mater* **2008**, *18*, 27-35.
- [3] H. Y. Chen, J. Lahann, *Adv Mater* **2007**, *19*, 3801-+.