Supporting Information

Copolymers Featuring Pentafluorophenyl Ester and Photolabile Amine Units: Synthesis and Application as Reactive Photopatterns

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Experimental section

Materials. All chemicals and solvents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF) was dried over sodium and freshly distilled before use. Triethylamine (Et_3N) was dried over calcium chloride and distilled previously. Poly(pentaflourophenyl acrylate) (PPFPA) was synthesized following a procedure described earlier[1] Piperazinyl-4-chloro-7-nitrobenzofuran (pip-NBD) was synthesized as reported.[2]

Instrumentation. ^{1}H- NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated solvents. The chemical shifts (δ) were given in ppm relative to trimethylsilane (TMS). Gel permeation chromatography (GPC) was used to determine the molecular weight and the corresponding

molecular weight distributions, (M_w/M_n), of the polymer samples with respect to polystyrene standards. GPC measurements were performed in THF. The flow rate was 1mL*min^{-1} at 25°C. IR spectra were recorded using a Bruker Vector 22 FT-IR spectrometer with an ATR unit. Fluorescence measurements were performed by using an inverted laser scanning microscope (Leica TCS SL) with an immersion objective (20). An argon laser (λ_{ex}=488 nm) was used for the excitation of pip-NBD. An Oriel LSH302 500W UV-lamp equipped with a 313 nm filter was used for UV-irradiation.

Photo-patterning of PPFPA-ONB and post-modification. A PPFPA-ONB solution (10 wt %) was spin-coated onto clean glass slides (15 s, 3000 rpm). An optical mask was tightly set up on the surface of the film and the samples were then exposed to UV light (313 nm, 500 W) irradiation for 3 h. After irradiation, the samples were immersed in dry THF for 1 hour to remove any non-crosslinked polymer. For a functionalization of the patterns, the samples were then immersed in a pip-NBD solution in THF at room temperature for 12h. To remove any excess of pip-NBD, the substrate was washed thoroughly with THF.

Synthesis of N,N'-dimethyl-N-(2-nitrobenzyl)ethane-1,2-diamine (1). A mixture of *N,N'-dimethylethane-1,2-diamine* (8.8g, 100 mmol, 5 equiv.) and K_2CO_3 (2.35g, 60 mmol, 3 equiv.) was stirred in acetone (15 mL) for 15 min at 50 °C. Then *1-(bromomethyl)-2-nitrobenzene* (4.3g, 20 mmol, 1 equiv.) was added dropwise. The mixture was stirred for 12 hours at 55 °C. Acetone was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with water. The organic phases were combined, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. A slightly brown liquid product (2.2 g, yield: 50%) was obtained by column chromatography (MeOH/NH_3 H_2O=100:1, volume ratio). ^{1}H NMR (δ, ppm, DMSO): 7.83 (d, 1H, ONB), 7.65 (m, 2H, ONB), 7.52 (t, 1H, ONB), 3.69 (s, 2H, ONB- (C***H***$_2$)N(CH$_3$)), 2.49 (t, 2H, -N(CH$_3$)*CH$_2$*CH$_2$N(CH$_3$)(H)), 2.37 (t, 2H, -N(CH$_3$)CH$_2$*CH$_2$*N(CH$_3$)(H)), 2.18 (-N(*CH$_3$*)CH$_2$CH$_2$N(CH$_3$)(H)), 2.02 (-N(CH$_3$)CH$_2$CH$_2$N*(CH$_3$)*(H)). ESI MS (*m/z*): calcd. for $C_{11}H_{17}N_3O_2$: 213.13; found: 214.13 $[M + H]^+$.

Synthesis of PPFPA-ONB (example, ONB content: 10 mol%). 600 mg (2.6 mmol) of PPFPA, 0.02 mL (0.26 mmol) of Et_3N and 56 mg (0.26 mmol) of compound **1** (correspond to 10% in respective to the pentafluorophenyl moieties) were dissolved in freshly distilled THF (5 mL). The mixture was stirred overnight at room temperature. The resulting polymer was isolated by precipitation into *n*-hexane and was then dried in vacuum. Yield: 410 mg of PPFPA-ONB. FT-IR: (cm^{-1}) 1750 (C=O) and 1520 (C-F). ^{1}H NMR (δ, ppm, $CDCl_3$): 7.8-7.2 (broad, proton in *o*-nitrobenzene), 3.2-1.2 (m, proton in backbone and linker of ONB).

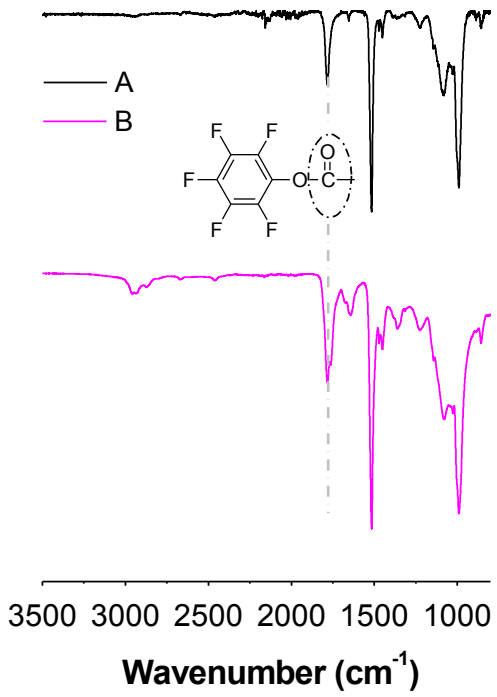

Figure S1. FT-IR for PPFPA (A) and PPFPA-ONB (ONB ratio, 10%) (B) after photo-crosslinking.

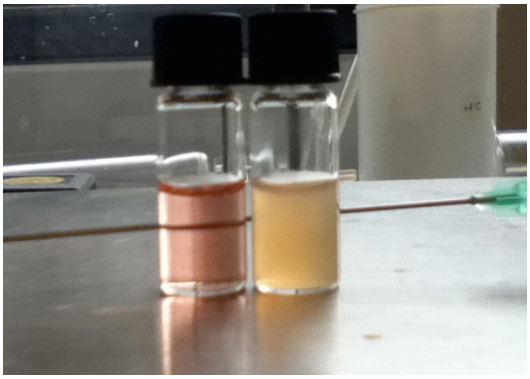

Figure S2. Photos for PPFPA (A) and PPFPA-ONB (ONB ratio, 10%) (B) after photo-crosslinking.

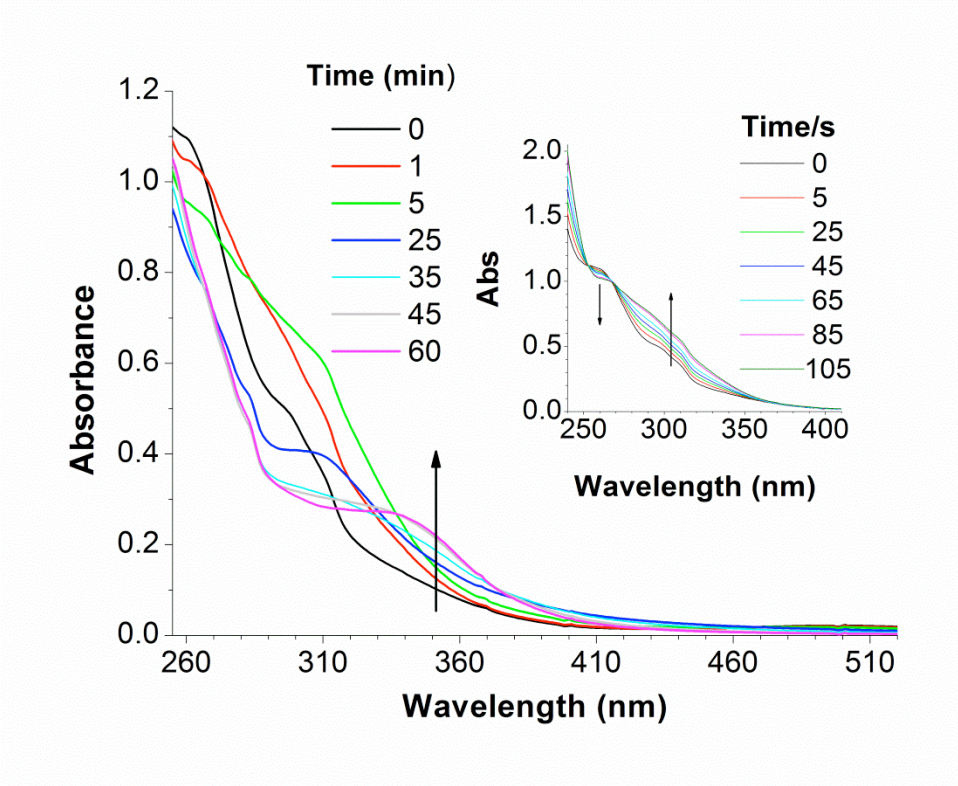

Figure S**3.** Irradiation (wavelength = 313 nm) time dependent UV spectra of PPFPA-ONB in THF. Concentration = 1 mg/mL.

1. F. D. Jochum and P. Theato, *Polymer*, 2009, **50**, 3079.
2. R. Nudelman, O. Ardon, Y. Hadar, Y. Chen, J, Libman and A. Shanzer, *J. Med. Chem*., 1998, **41**, 1671.