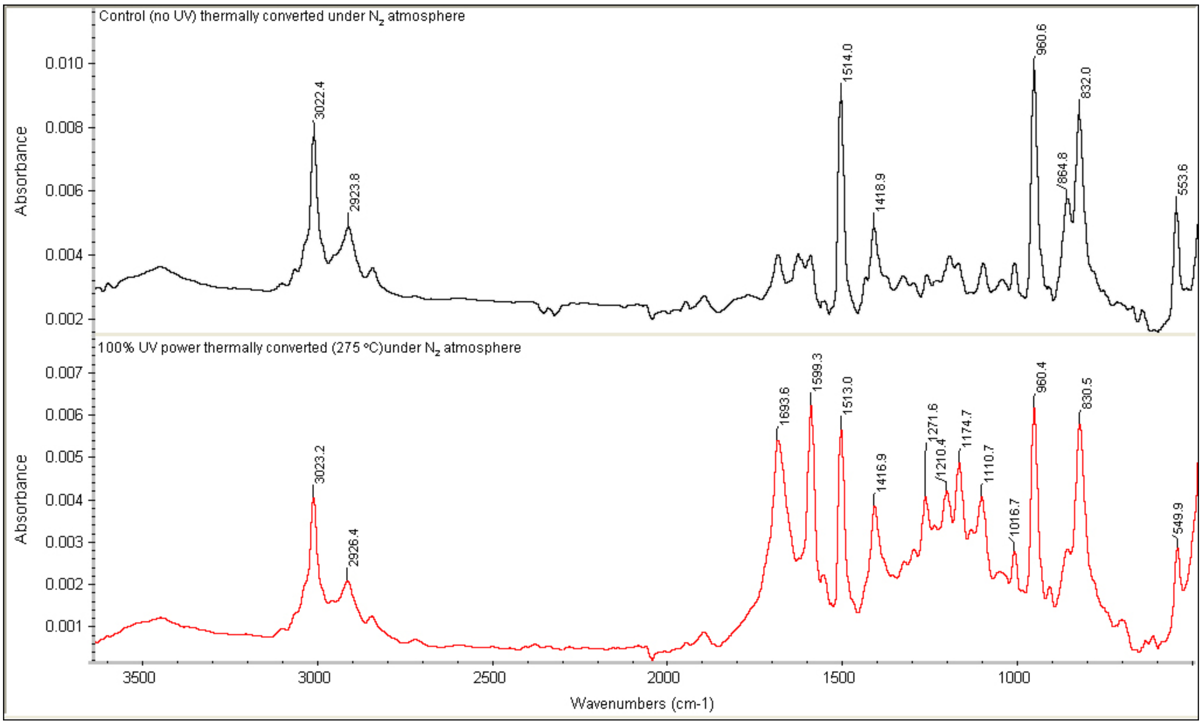
Supporting Information

UV-Vis spectroscopy was performed using a Perkin Elmer Lambda 950 UV/Vis spectrometer. The UV-light source used for UV dosage studies and photolithography was a Fusion UV system model I6B. A collimated deep UV (280 – 310 nm) light source (AMB, Inc. ST100) was also used for photolithography. Film thickness measurements were performed using a Dektak IIA profilometer or a KLA Tencore model P-15 profilometer.

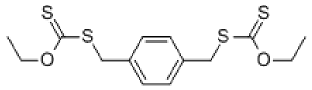
X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD with monochromatic Al Ka excitation (1486.6 eV). The analyzed spot size was 300x700 micrometers and chamber base pressures were less than $5x10^{-9}$ Torr. Survey spectra were taken with Pass Energy 80, 200 ms dwell times, and 1 eV steps. High resolution core level spectra were recorded with a pass energy 20 and 0.1 eV steps. Quantification and data fitting were performed with CasaXPS software.

FTIR was performed using a Thermo Nicolet 6700 spectrometer using Thermo KBr 25 x 4 mm discs. A solution of the polymer (2.5% w/w in dichloroethane) was spin-coated onto KBr discs (1,500 RPM). The samples were heated to 100 °C for 5 min, and one of the samples was run through the Fusion UV system at 100% power. The samples were thermally converted (275 °C) under a N_2 atmosphere and the FTIR spectra were recorded. FTIR spectra were consistent with (and based on) previous literature reports.[1,2] Control: wavenumbers (cm^{-1}) 3022 (trans-vinylene CH stretch), 2924 (aliphatic CH stretch), 1514, 1419 (‘semi-circle’ ring stretch), 961 (trans-vinylene CH out-of-plane bend), 865 (cis-vinylene CH out-of-plane bend) 832 (*p*-phenylene CH out-of-plane bend), 554 (*p*-phenylene out-of-plane ring bend). 100% UV power: wavenumbers (cm^{-1}) 3023 (trans-vinylene CH stretch), 2926 (aliphatic CH stretch), 1694 (carbonyl stretch), 1599 (substituent perturbation of *p*-phenylene ring)[2], 1513, 1417 (‘semi-circle’ ring stretch), 1271, 1175, 1111 (*p*-phenylene CH in-plane bend), 1210 (vinylene CH in-plane bend) 960 (trans-vinylene CH out-of-plane bend), 830 (*p*-phenylene CH out-of-plane bend), 550 (*p*-phenylene out-of-plane ring bend).

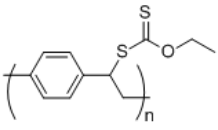


Synthesis of the ethylxanthate monomer and polymer were based off a previous literature report.[3] All chemicals were purchased from Fisher Scientific and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker model DRX400 or Bruker AVANCE 500 spectrometer. Proton and carbon chemical shifts are reported relative to the solvent, which was used as an internal standard. Anhydrous THF and t-BuOK (1.0 M in THF) were purchased in AcroSeal bottles. Precursor polymers were isolated using a Fisher Scientific centrifuge operating at 6,000 rpm. GPC analysis was performed on a Polymer Labs 220 PL-GPC equipped with two columns operated in series: a PLgel 5μm MiniMIC-C (250mm x 4.6mm) and a PLgel 5 μm

MiniMIX-C (50mm x 4.6mm) guard column. Chloroform was used as the eluent (0.4 mL/min), and measurements were performed at 35 °C. Calibration was performed using polystyrene standards with narrow molecular weight distributions (Fluka ReadyCal 400-2,000,000).



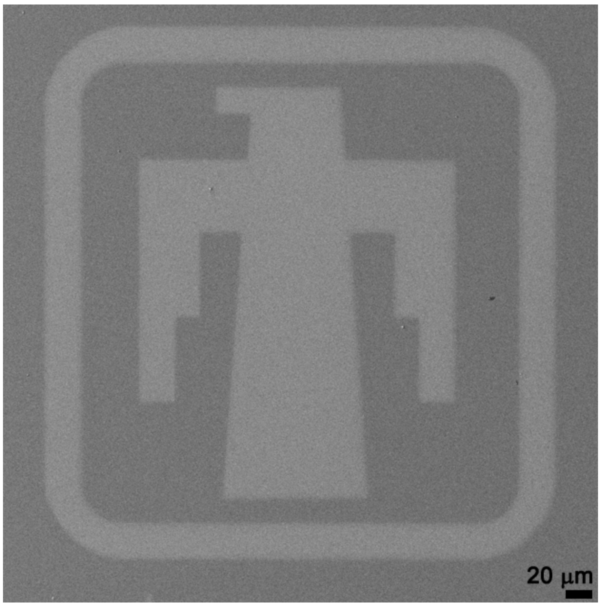
Synthesis of bis-ethylxanthate monomer. A solution of 1,4-bis(chloromethyl)benzene (8.29 g, 47.4 mmol) and *O*-ethoxyxanthic acid potassium salt (18.97 g, 118.4 mmol) were vigorously stirred in methanol (700 mL) at 40 °C for 24 h. Approximately half of the solvent was evaporated under reduced pressure (rotovap) and distilled H_2O (150 mL) was added to the mixture and stirred for 5 min. The precipitate was isolated by vacuum filtration and dried under vacuum. The desired compound was obtained without further purification as a white solid (13.22 g, 80%). mp = 115-116 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27 (4 H, s), 4.63 (2H, q, *J* = 7.2 Hz), 4.32 (4H, s), 1.40 (6H, t, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 214.1, 135.3, 129.5, 70.3, 40.2, 14.0.

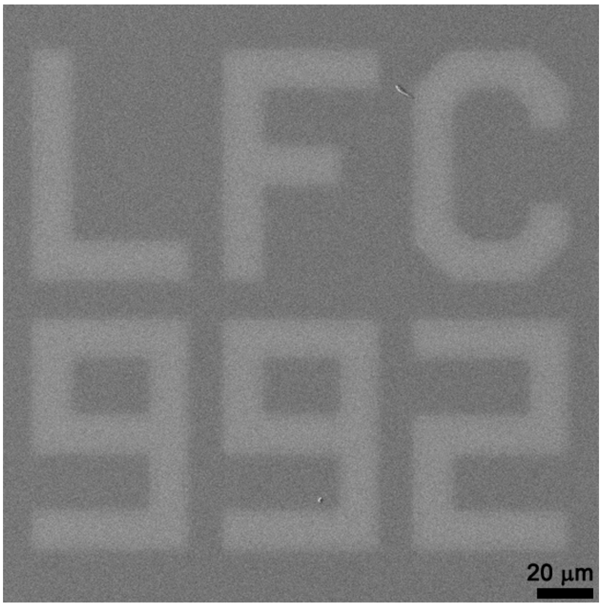


Synthesis of ethylxanthate polymer. To a stirred solution of monomer (4.85 g, 14.0 mmol) in anhydrous THF (100 mL) at 0 °C was added t-BuOK (14.0 mL, 1.0 M in THF) under a N_2 atmosphere. After 5 min of stirring, the ice bath was removed. The reaction was stirred for 1 h and poured over a stirring ice-water bath. The aqueous layer was extracted with chloroform (4 x 100 mL) and the combined organic fractions were dried over Na_2SO_4. The solvent was evaporated (rotovap) until ~100 mL remained, and the solution was poured over cold 1:1 hexanes/diethyl ether (400 mL). The mixture was transferred to centrifuge tubes and spun down. The product was isolated and dried under vacuum (1.79 g, 57%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.01-6.84 (4H), 4.80 (1H), 4.51 (2H), 3.27 (1H), 3.05 (1H), 1.29 (3H). FT-IR (KBr, cm^{-1}) 2982, 1512, 1217, 1146, 1110, 1048. The number and weight average molecular weight of the precursor polymer was 51,855 and 119,633 with a polydispersity index of 2.31.

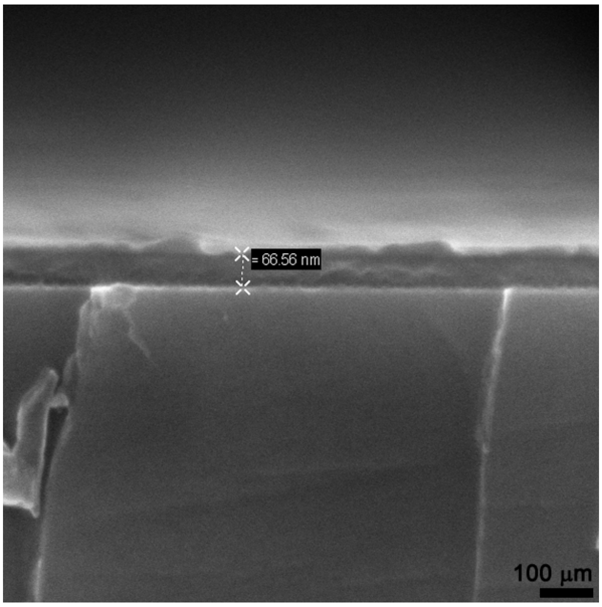
DC conductivity measurements were performed using a Keithley 6485 picoammeter with an Agilent E4980 LCR meter as the DC power supply. The polymer samples (2.5% w/w in $CHCl_3$) were deposited onto 5 µm spaced interdigitated electrodes (made in house). Measurements were taken under ambient conditions in the dark (to suppress photoconductivity). IV sweeps from 0-2 volts were performed and the measured current was used to calculate the specific resistance, and subsequently, the conductivity of the samples.

SEM images were recorded using a Zeiss Supra 55VP field emission scanning electron microscope. Samples were imaged using 5kV accelerating voltage.

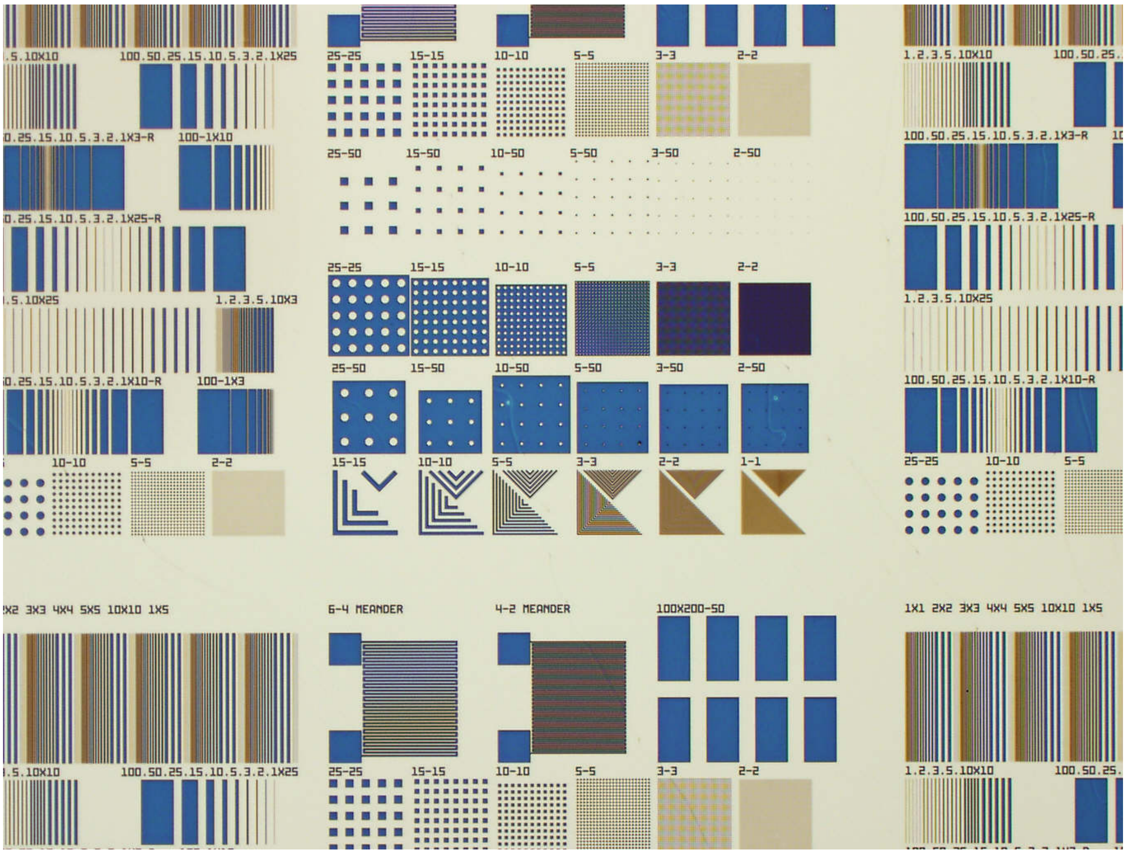




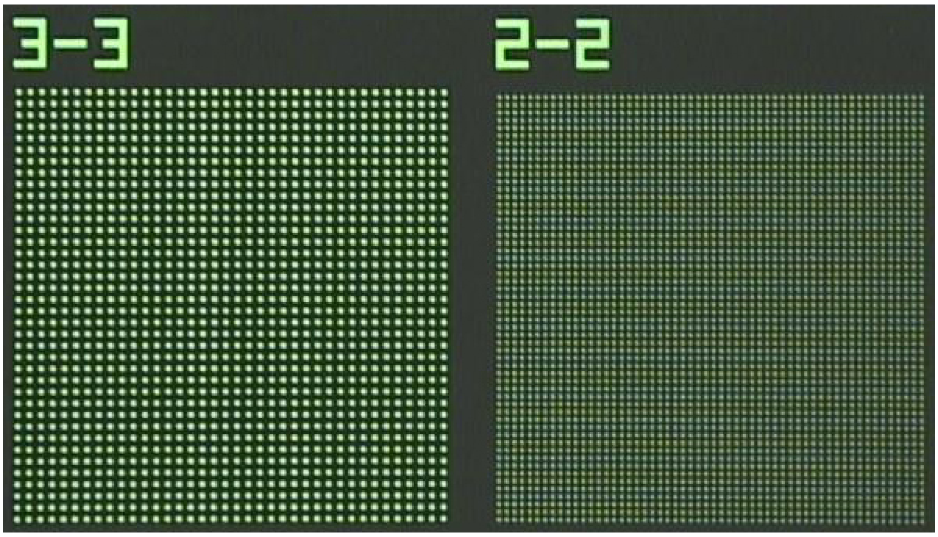
An edge-on view of the polymer film was taken by freeze-fracturing a photo-patterned polymer film on a silicon substrate. The image shows a film with a measured thickness of ~66 nm, in agreement with Dektak measurements.

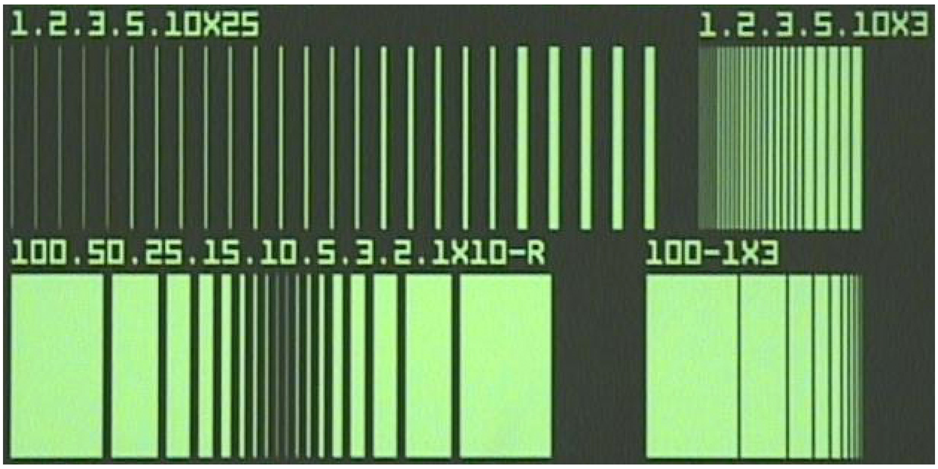


Optical images were recorded either using a Clear Focus imaging system, which utilizes a Wesco DZ2 zoom microscope and a QImaging micropublisher 5.0 RTV camera or an Olympus MX80 microscope. The image below shows photopatterned PPV polymer from a Microfab qualification mask. The numbers indicate the feature size and spacing (in microns).

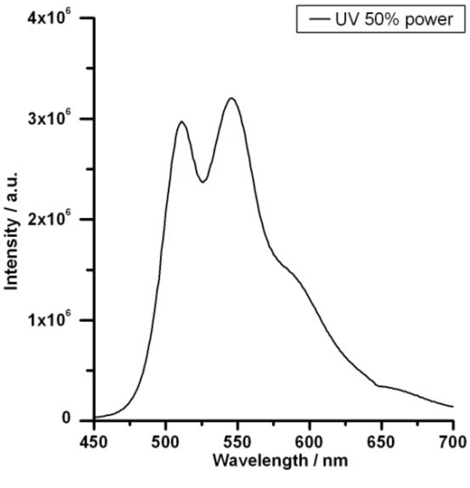


Fluorescence microscopy was performed using a Leica INM 200 microscope with a H3 filter and an excitation mode between 420 – 490 nm. The numbers indicate the feature size and spacing (in microns).





Fluorescence spectroscopy was performed using a Fluorolog FL3 spectrofluorimeter in “front face” mode with both the entrance and exit slits set to a 2 nm band pass and an excitation wavelength of 400 nm. A thin film sample was prepared as previously described in the UV-Vis study, subjected to 50% power from the Fusion UV system, and thermally converted (30 min at 275 °C under a N_2 atmosphere). The spectrum recorded had a similar profile to previous literature reports.[4]



References

1. D. D. C. Bradley, *J. Phys. D.*, 1987, **20**, 1389.
2. F. Papadimitrakopoulos, K. Konstadinidis, T. M. Miller, R. Opila, E. A. Chandross and M. E. Galvin, *Chem. Mater.*, 1994, **6**, 1563.
3. E. Kesters, S. Gillissen, F. Motmans, L. Lutsen and D. Vanderzande, *Macromolecules*, 2002, **35**, 7902.
4. S. Heun, R. F. Mahrt, A. Greiner, U. Lemmer, H. Bassier, D. A. Halliday, D. D. C. Bradley, P. L. Burns and A. B. Homes, *J. Phys.: Condens. Matter*, 1993, **5**, 247.