Table 1 UVB (280-320 nm) exposure and XPS data

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

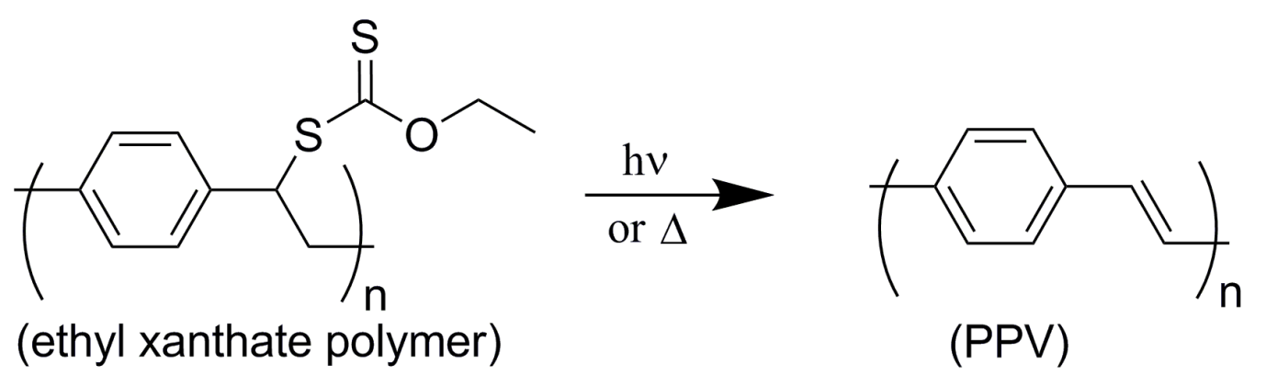
Photopatterning of Precursor Poly(*p*-phenylenevinylene) Polymers

Ross S. Johnson,[1] Jacob J. Haworth,[1] Patrick S. Finnegan,[1] David R. Wheeler[2] and Shawn M. Dirk[1]

Sandia National Laboratories, Organic Materials Department [1] Biosensors and Nanomaterials [2]

Introduction

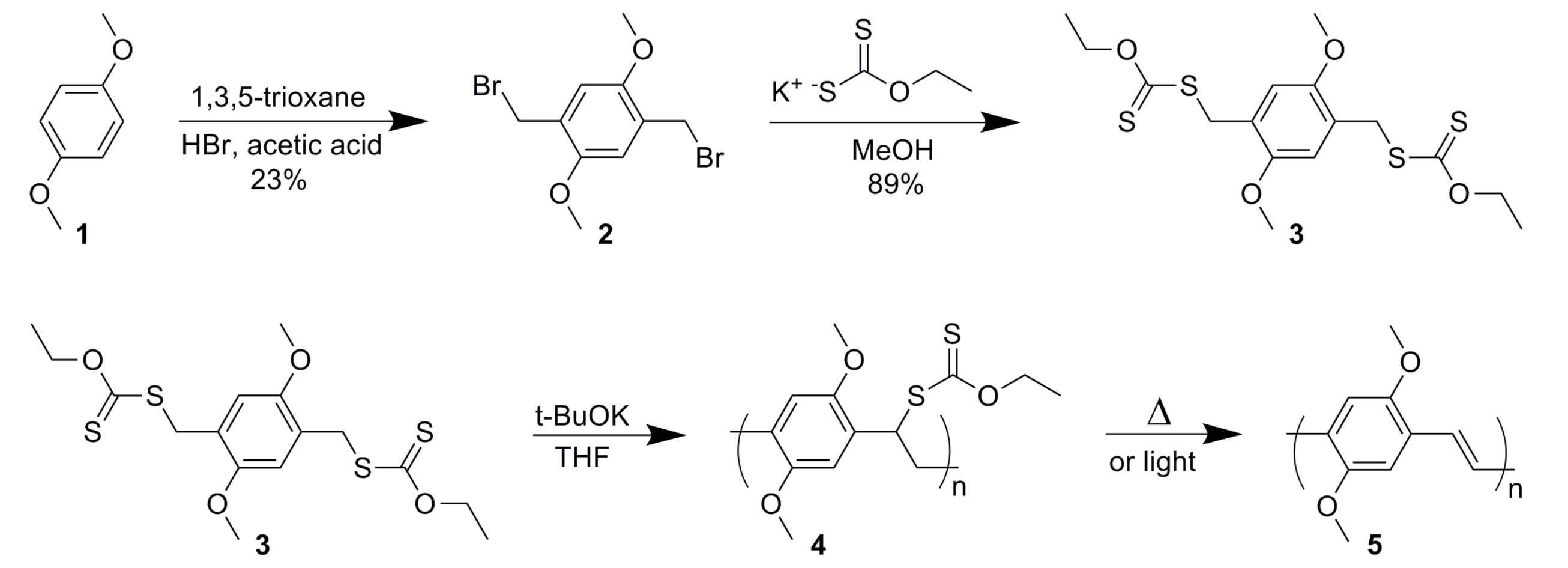
Conjugated polymers are commonly utilized in electronic and optoelectronic devices. The ability to control the lateral spatial resolution of conjugated polymers will allow for improved integration into future devices. We have previously described[1] a method for photopatterning a xanthate precursor polymer leading to micron scale spatial control of conjugated poly(*p*-phenylenevinylene). Here, we expand on our initial work, examining the photopatterning of two xanthate precursor polymers with improved conductivity.



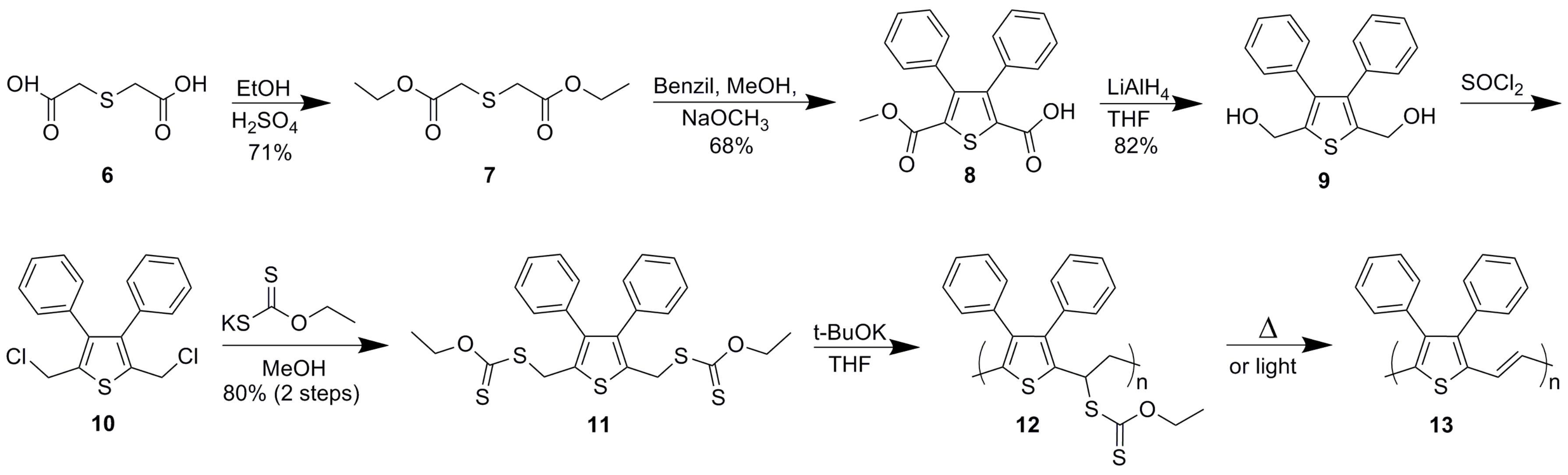
[1] Johnson et al. *Chem. Commun.* **2011**, *47*, 3936-3938.

Synthesis

The dimethoxy xanthate precursor polymer **4** was prepared in three steps.

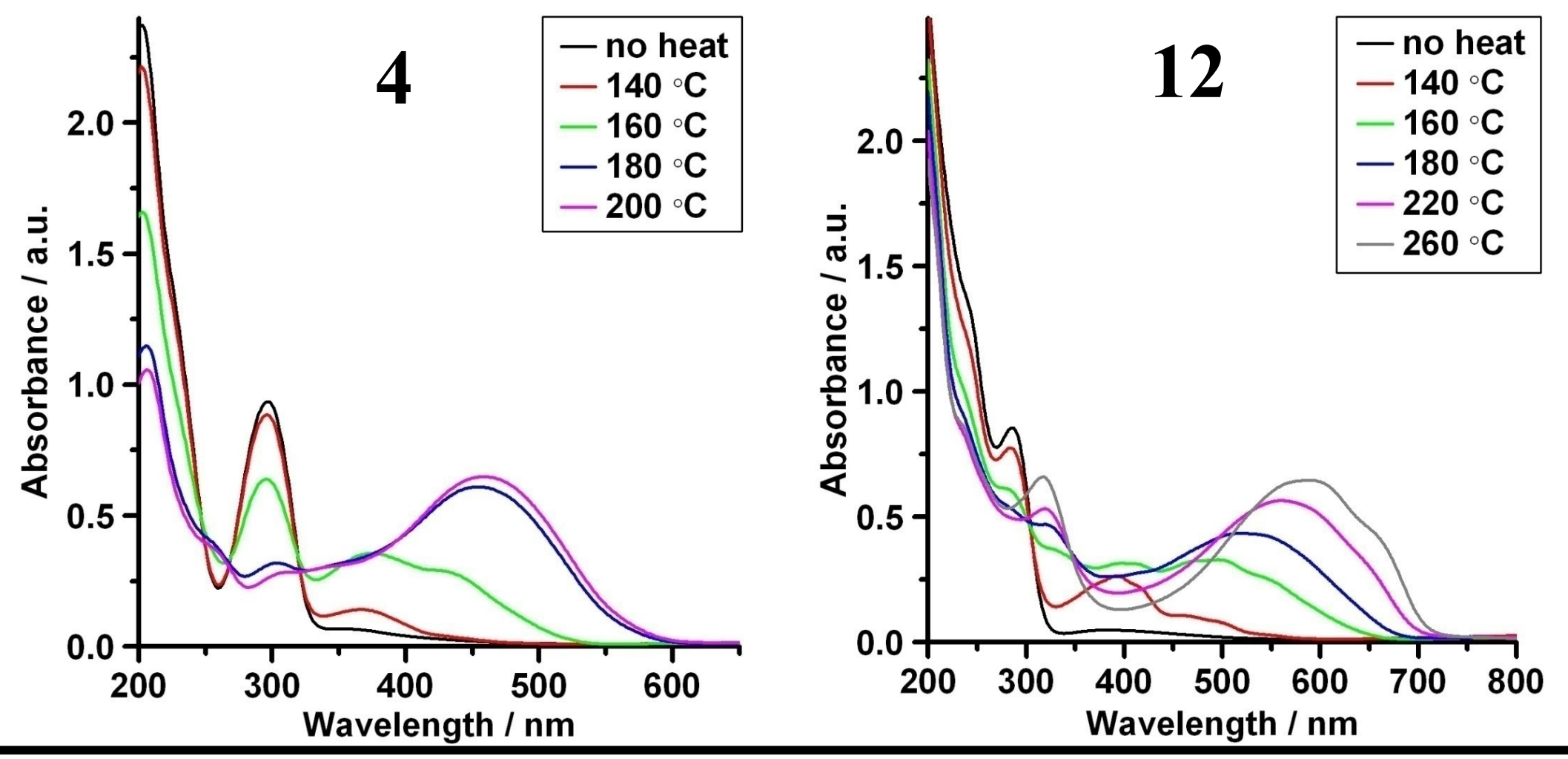


The thiophene xanthate precursor polymer **12** was synthesized in six steps.



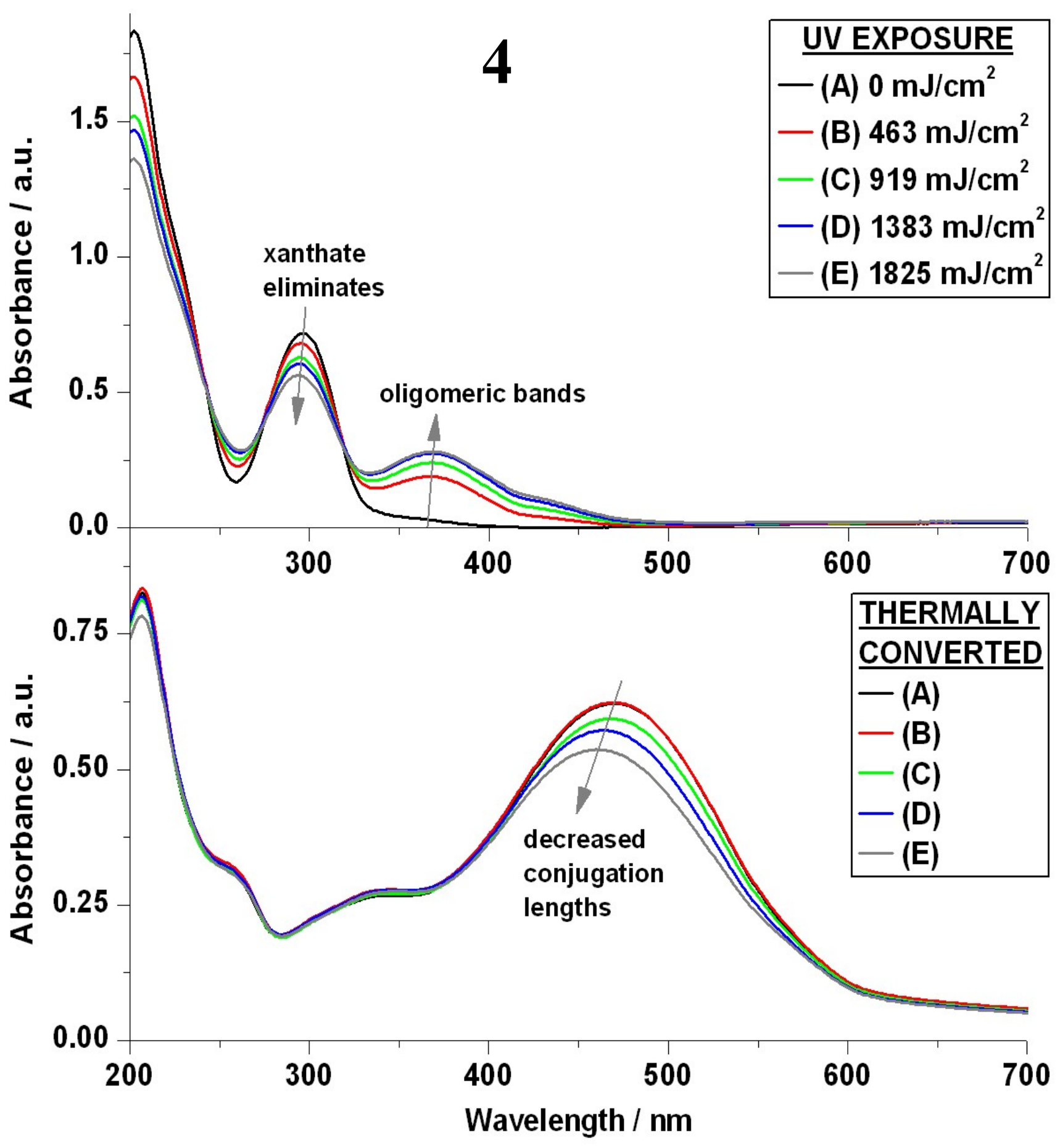
UV Characterization

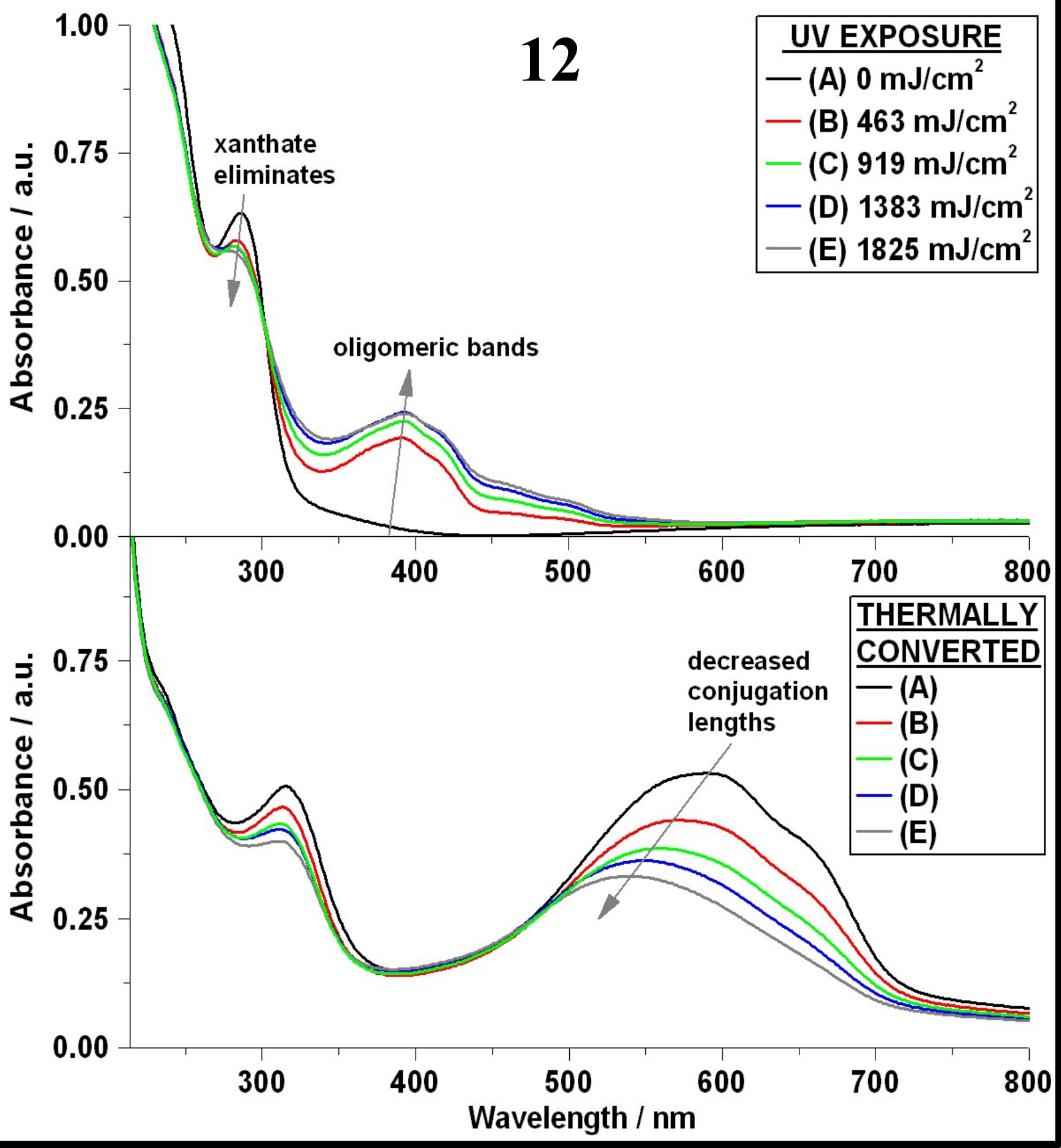
The dimethoxy polymer **4** had a λ_{max} of 460 nm after heating the polymer to 200 °C while the thiophpene polymer **12** displayed a λ_{max} of 587 nm after heating the polymer to 260 °C. Both polymers are significantly red-shifted compared to PPV.



Optimizing Exposure

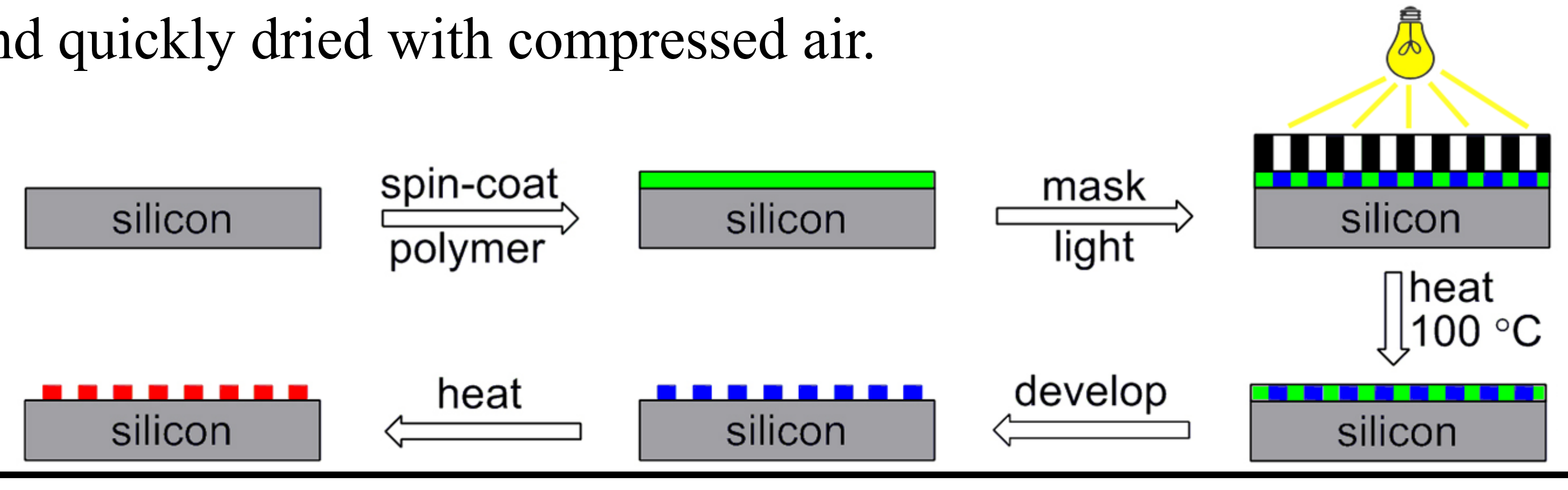
A dosage study was performed to determine the effects of UV-light exposure on the precursor polymers. Dilute solutions of the polymers were spin-coated onto 1x1 inch quartz slides and the samples were exposed to varying dosages of UV light. High exposure levels reduced conjugation lengths (after thermal treatment). The dimethoxy analogue was much less affected by UV-light.





Photopatterning Process

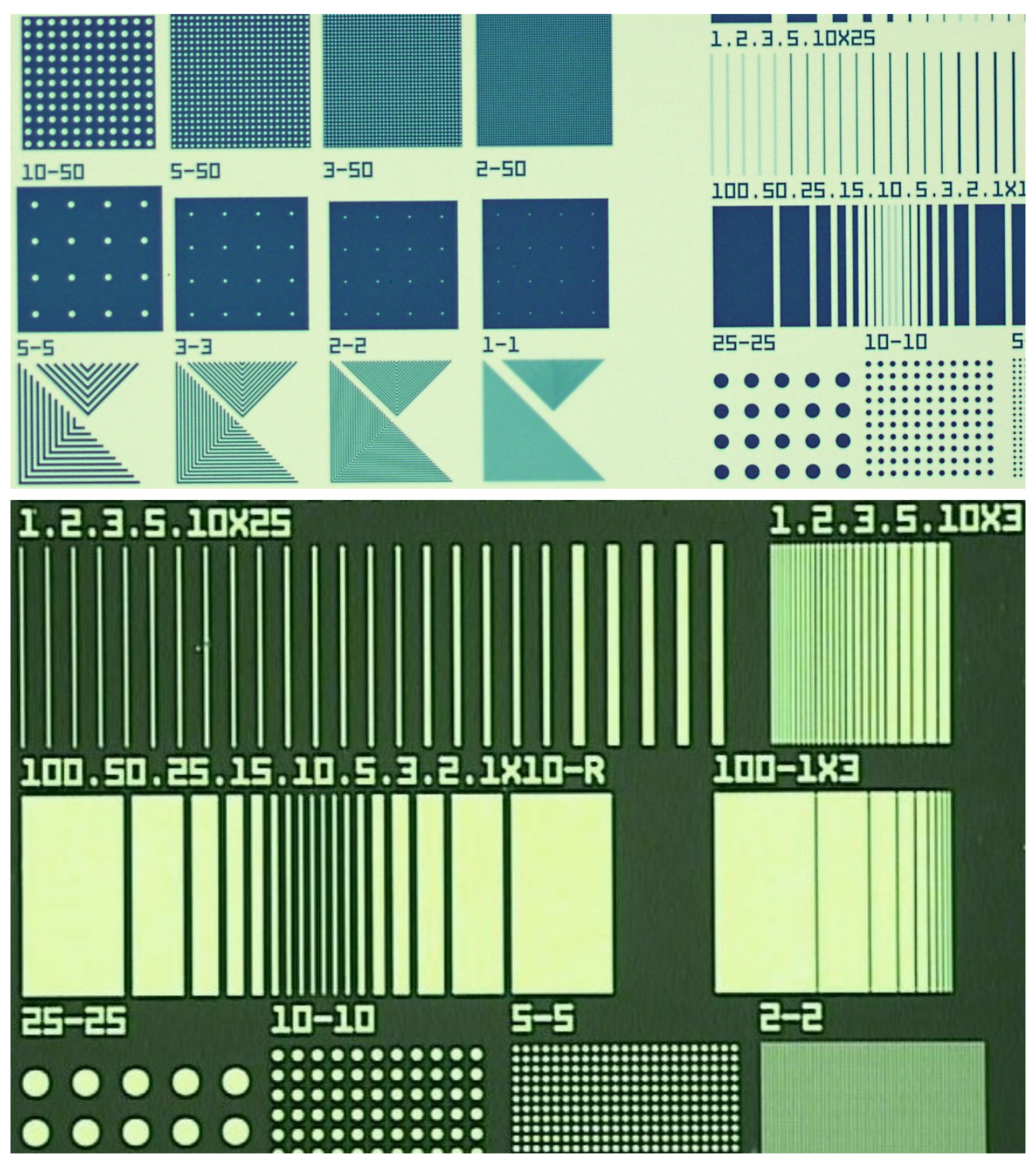
Solutions of the polymer (2.0% w/v in dichloroethane) were spin-coated onto silicon wafers. A soft-bake (100 °C for 3 min) was performed to remove residual solvent. A mask was placed over the substrate and the samples were exposed to deep UV light (280-310 nm) from a collimated source. A second soft-bake (100 °C for 3 min) was performed to remove CS_2 and EtOH produced from the elimination reaction. Samples were developed by submerging the substrates in solvent for 10 seconds and quickly dried with compressed air.



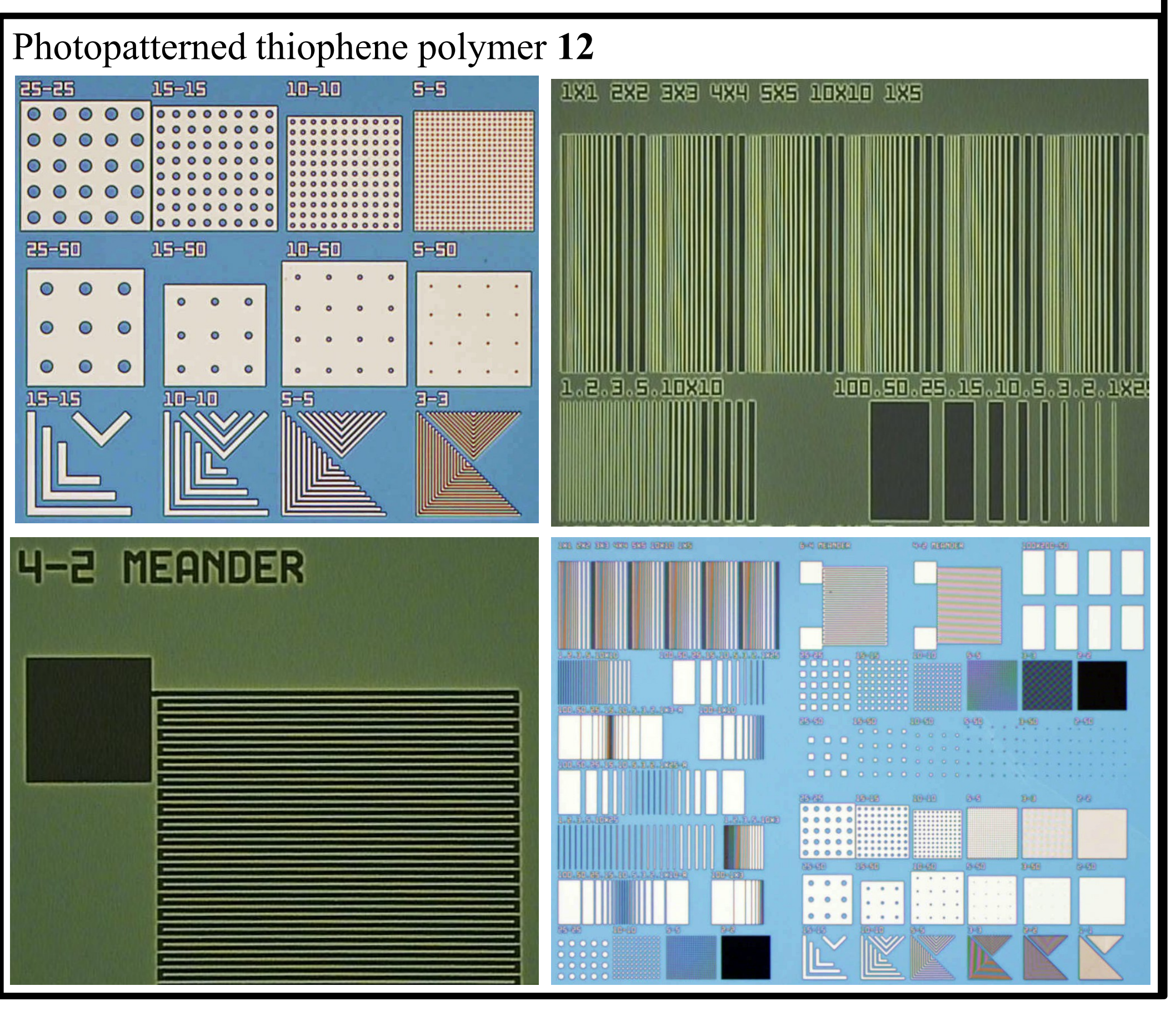
Optical and Fluorescence Imaging

Optical and fluorescence microscopy revealed a uniform polymer film with lateral feature sizes ranging from as small as 1 µm up to several millimeters, indicating the mask features were reproduced with high-fidelity. The dimethoxy polymer **4** initially appeared to be a negative tone resist, but further analysis and optimization of the developing conditions are needed. The thiophene polymer **12** was unexpectedly found be a positive tone resist (areas exposed to light washed away).

Photopatterned dimethoxy polymer **4**

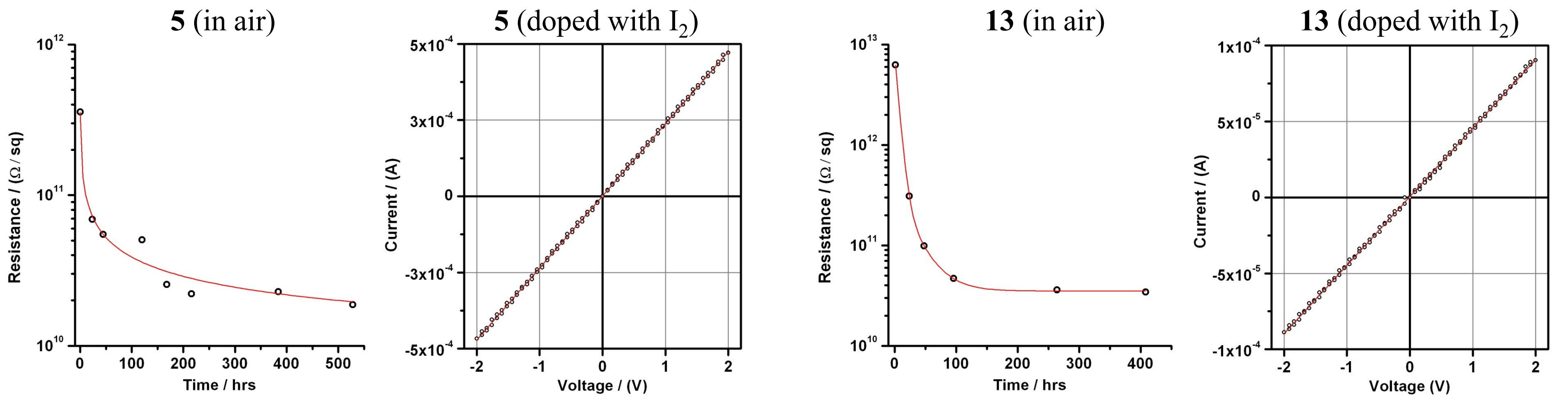


Photopatterned thiophene polymer **12**



Resistivity

The polymers were deposited onto quartz substrates containing gold pads of known dimension and spacing. IV traces were recorded as a function of time in air, and after doping with I_2 vapor for 24 hours. The dimethoxy polymer **5** displayed a sheet resistance of 2^{10} Ω/sq after 22 days in air which decreased to 4^3 Ω/sq after I_2 doping. The thiophene polymer **13** displayed a sheet resistance of 3^{10} Ω/sq after 17 days in air which decreased to 2^4 Ω/sq after I_2 doping.



Conclusions

We have demonstrated that xanthate precursor polymers can be photopatterned with micron-scale resolution. Because the dimethoxy polymer **4** is not greatly affected by UV light, and the thiophene polymer **12** is a positive tone resist, the conductivity of the patterned material will not be affected by the patterning process. Further work will be needed to optimize the developing conditions of **4** as well as understand the chemistry behind the patterning of **12**. Future work will attempt to utilize the improved spatial control to incorporate these and other conjugated polymers into electroluminescent and electronic devices.

National Nuclear Security Administration

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