



---

**Polymeric and Molecular Materials for Advanced Organic Electronics**

**TOBIN MARKS  
NORTHWESTERN UNIVERSITY**

---

**07/27/2018  
Final Report**

**DISTRIBUTION A: Distribution approved for public release.**

**Air Force Research Laboratory  
AF Office Of Scientific Research (AFOSR)/ RTB2  
Arlington, Virginia 22203  
Air Force Materiel Command**

DISTRIBUTION A: Distribution approved for public release

<b>REPORT DOCUMENTATION PAGE</b>			<i>Form Approved</i> <i>OMB No. 0704-0188</i>		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p><b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</b></p>					
<b>1. REPORT DATE (DD-MM-YYYY)</b> 27-07-2018		<b>2. REPORT TYPE</b> Final Performance		<b>3. DATES COVERED (From - To)</b> 01 Mar 2015 to 28 Feb 2018	
<b>4. TITLE AND SUBTITLE</b> Polymeric and Molecular Materials for Advanced Organic Electronics			<b>5a. CONTRACT NUMBER</b>		
			<b>5b. GRANT NUMBER</b> FA9550-15-1-0044		
			<b>5c. PROGRAM ELEMENT NUMBER</b> 61102F		
<b>6. AUTHOR(S)</b> TOBIN MARKS, Antonio Facchetti			<b>5d. PROJECT NUMBER</b>		
			<b>5e. TASK NUMBER</b>		
			<b>5f. WORK UNIT NUMBER</b>		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> NORTHWESTERN UNIVERSITY 633 CLARK ST EVANSTON EVANSTON, IL 60208-0001 US			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203			<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> AFRL/AFOSR RTB2		
			<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-AFOSR-VA-TR-2018-0281		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> A DISTRIBUTION UNLIMITED: PB Public Release					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> To realize high-performance organic/polymeric/hybrid materials and devices and to address the challenges hindering the progress of printed, flexible, stretchable electronics, it will first be necessary to develop new materials (semiconductors, gate dielectrics, conductive contacts), understand/optimize critical coating/printing processes, study materials interfaces affecting charge injection (contact-semiconductor) and transport (dielectric-semiconductor) as well as to understand/model charge transport and mechanical response in these unconventional devices. Before detailing the proposed research and deliverables, we summarize results from the previous Northwestern (NU) AFOSR-supported program. Significant advances were possible through the highly productive and close collaboration between other NU specialists, other NU faculty, as well as collaborations involving other academic groups (e.g., Stanford U., U. of Illinois Urbana-Champaign, U. of Minnesota, Nat. Central U. of Taiwan, U. of Malaga in Spain, U. Groningen in Holland, Purdue U., U. Cal. Santa Barbara, University College London, South China U. of Sci. & Tech., and Cambridge U.), national laboratories (Argonne Nat. Lab., AFRL, NIST, NRL), and our nearby industrial transition partners (Polyera Corp., Flexterra Corp.).					
<b>15. SUBJECT TERMS</b> Organic electronics, organic transistor, flexible electronics, organic bipolar semiconducting materials					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b> CASTER, KENNETH
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			
Unclassified	Unclassified	Unclassified	UU		

Standard Form 298 (Rev. 8/98)  
Prescribed by ANSI Std. Z39.18

DISTRIBUTION A: Distribution approved for public release

				<b>19b. TELEPHONE NUMBER</b> <i>(Include area code)</i> 703-588-8487
--	--	--	--	-------------------------------------------------------------------------

## Polymeric and Molecular Materials for Advanced Organic Electronics

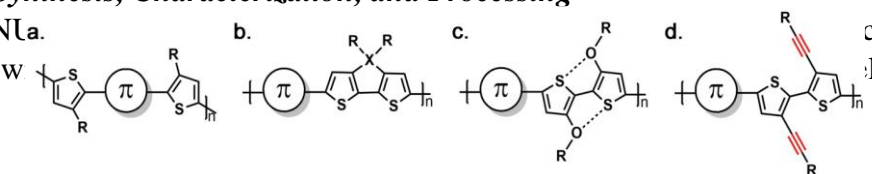
To realize high-performance materials and devices and to address the challenges hindering the progress of printed, flexible, stretchable electronics, it will first be necessary to develop new materials (semiconductors, gate dielectrics, conductive contacts), understand/optimize critical coating/printing processes, study materials interfaces affecting charge injection (contact-semiconductor) and transport (dielectric-semiconductor) as well as to understand/model charge transport and mechanical response in these unconventional devices. Before detailing the proposed research and deliverables, we summarize results from the previous Northwestern (NU) AFOSR-supported program. Significant advances were possible through the highly productive and close collaboration between other NU specialists, other NU faculty, as well as collaborations involving other academic groups (e.g., Stanford U., U. of Illinois Urbana-Champaign, U. of Minnesota, Nat. Central U. of Taiwan, U. of Malaga in Spain, U. Groningen in Holland, Purdue U., U. Cal. Santa Barbara, University College London, South China U. of Sci. & Tech., and Cambridge U.), national laboratories (Argonne Nat. Lab., AFRL, NIST, NRL), and our nearby industrial transition partners (Polyera Corp., Flexterra Corp.). These collaborations represent a powerful leveraging capability, and involve frequent exchanges of samples and the application of characterization and computational capabilities well beyond any a single research group. At times these interactions capitalize on jointly supervised graduate or postdoctoral students who bring new skills to the AFOSR effort. Furthermore, the NU AFOSR-sponsored program has benefited from students with graduate (e.g., NSF, NDSEG) and postdoctoral (Dreyfus, Marie Curie) fellowships, and many international scholars who were supported by their home countries, such as Italy, Spain, Taiwan, China, Korea, India, Portugal, and Sweden, to name a few. The world-class materials characterization facilities at NU also add great strength to the AFOSR program. ***All of these collaborations and assets have been crucial to achieving program objectives with maximum effectiveness and will continue in this mode for future efforts.***

### 1. Organic Semiconductor Synthesis, Characterization, and Processing

architectures. This work was motivated by the fact that organic semiconductors for TFTs, with

exhibiting high mobility and current modulation in air are crucial to achieving high-speed low power organic CMOS (complementary) circuits, where high-performance p- and n-type transistors must

be developed and integrated. However we also elucidate those processing strategies that afford optimum microstructures for charge mobility. Over the past project period, the four central focal points were: *i*) new ways to manipulate aromatic juncture coplanarity (enhance  $\pi$ -carrier mobility) in semiconducting polymers while maintaining solubility and processability; *ii*) exploring new  $\pi$ -systems for semi-conducting polymers; *iii*) exploring new, generalizable, green synthetic routes to semiconducting polymers that avoid large quantities of toxic reagents; *iv*) realizing the potential of polymer-polymer blends and ternary materials.

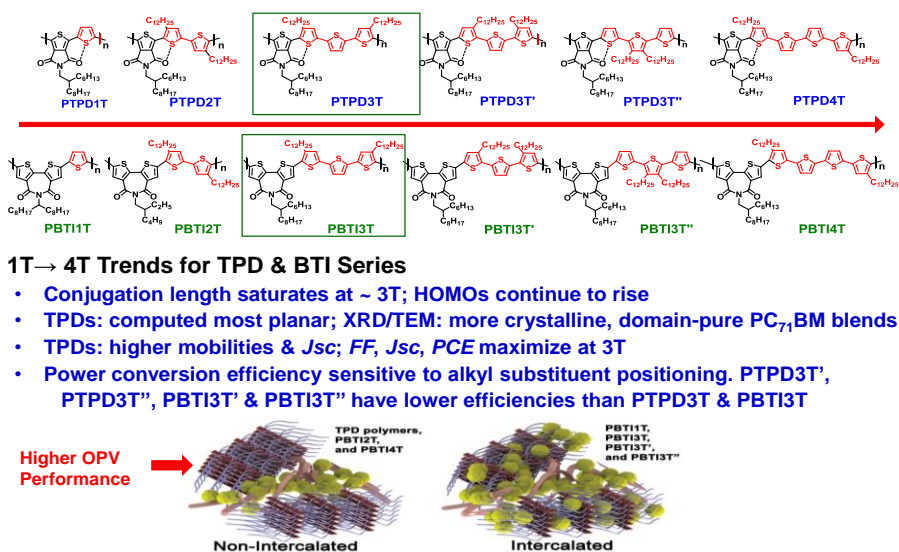


**Fig. 4.** Materials design strategies for polymer semiconductors with high degrees of backbone coplanarity: (a) inserting non-alkylated  $\pi$ -spacers; (b) conformational locking through covalent bonds; (c) conformational locking through intramolecular non-covalent interactions; (d) introducing “slim” alkynyl side chains. Incorporating sp hybridized C centers to reduce steric hindrance and promotes backbone planarity.

For focus *i*, several strategies are in principle possible to force adjacent aromatic rings into coplanarity for maximum  $\pi$ -delocalization (Fig. 4). We have explored strategies that allow some torsional motion to enhance solubility/processability but then “freeze” into coplanarity when the films are solidified (**4c** and **4d**). The “conformational locking” in **4c** with weak covalent interactions allows us to create families of extensively characterized (NMR, X-ray scattering, TGA/DSC, TEM, optical, TFT, SCL transport, OPV, CV, UPS, electronic structure computation) polythiophene donor-acceptor copolymers and to elucidate structure-property relationships (Fig. 5). In collaborative work aimed at characterizing opto-electronic properties, we find in collaboration with photovoltaic specialists that the members of the conformationally-locked series have excellent solubility/film-forming properties, and exceptional photovoltaic metrics, including high power conversion efficiencies and record fill-factors, which are metrics of our ability to control charge and exciton flow in donor-acceptor binaries and ternaries. Strategy **4c** is a sterically-based strategy which places  $sp$ -hybridized, non-bulky solubilizing alkynyl substituents at thiophene  $\beta$ -positions. The result is a family of  $\pi$ -coplanar, readily processable polymers with good TFT mobilities because *alkyl*thiophene steric repulsions which would normally twist the thiophene planes are minimized in *alkynyl*-thiophenes.

Focus *ii* explores a completely new connectivities for organic semiconductors, using diyne ( $-C\equiv C-C\equiv C-$ ) linkages to impart combined torsional freedom while maintaining essentially uninterrupted  $\pi$ -delocalization, and offering the intriguing possibility of post-polymerization crosslinking via the diyne units (Fig. 6). The synthetic strategy we developed yields a family of processable macro-molecules having useful molecular masses, good film-forming characteristics, and extended  $\pi$ -conjugation as judged by optical and opto-electronic metrics. These include good TFT mobilities and solar cell power conversion efficiencies.

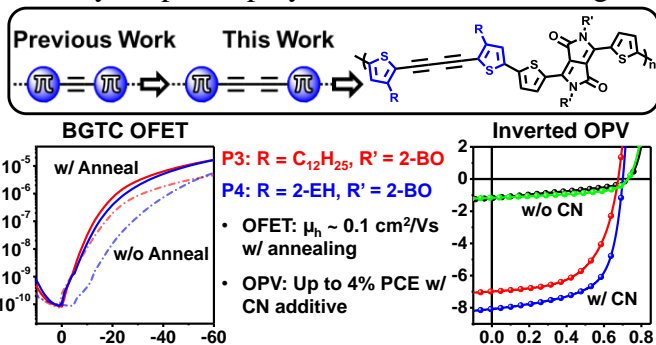
Focus *iii* addresses the important issue of whether green, environmentally benign synthetic routes to high-performance  $\pi$ -



#### 1T → 4T Trends for TPD & BTI Series

- Conjugation length saturates at ~ 3T; HOMOs continue to rise
- TPDs: computed most planar; XRD/TEM: more crystalline, domain-pure PC<sub>71</sub>BM blends
- TPDs: higher mobilities & *J*<sub>sc</sub>; FF, *J*<sub>sc</sub>, PCE maximize at 3T
- Power conversion efficiency sensitive to alkyl substituent positioning. PTPD3T', PTPD3T'', PBTI3T' & PBTI3T'' have lower efficiencies than PTPD3T & PBTI3T

**Fig. 5.** Comparison of thiophene (T) extension effects on opto-electronic properties in donor-acceptor polymeric systems with conformational locking (TPD, top) and without conformational locking (BTI, bottom) to stabilize  $\pi$ -system coplanarity.

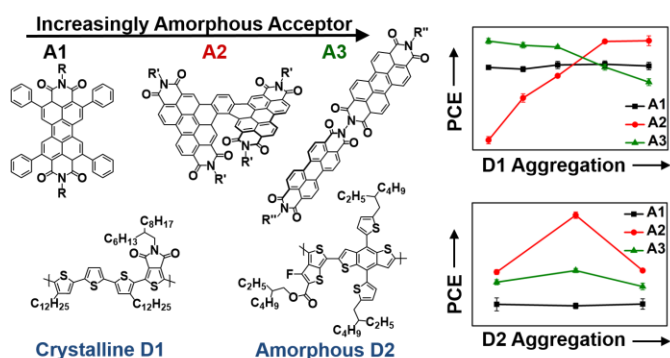


**Fig. 6.** Polymeric semiconductors employing torsionally flexible butadiyne linkages have good OFET mobilities and OPV power conversion efficiencies.



Specifically, increasing  $M_n$  for both polymers shrinks blend film domain sizes and enhances donor-acceptor polymer-polymer interfacial areas, affording increased photovoltaic short-circuit current densities ( $J_{sc}$ ). However, the greater disorder and intermixed feature proliferation accompanying increasing  $M_n$  promotes charge carrier recombination, reducing cell fill factors ( $FF$ ). The optimized photo-active layers exhibit well-balanced exciton dissociation and charge transport characteristics, ultimately providing OPVs with a two-fold efficiency enhancement versus devices with non-optimal  $M_n$ s. Importantly, proper, precise tuning of both donor and acceptor polymer  $M_n$ s is critical to optimize APSC performance. In contrast to reports where maximum power conversion efficiencies (PCEs) are achieved for the highest  $M_n$ s, the present 2-D  $M_n$  optimization matrix strategy locates a “sweet spot” at intermediate  $M_n$ s of both donor and acceptor polymers, a result which is well-explained by the coarse-grain modeling. This study also provides synthetic methodologies to precisely “dial in” conjugated polymers with desired  $M_n$  values and highlights the importance of optimizing  $M_n$  of *both* components to realize the full potential of blend performance. The reason for this “sweet spot” could be seen in the coarse grain modeling.

In related work we systematically investigated perylene-3,4,9,10-tetracarboxylic diimide (PDI) small molecule acceptor (SMA) crystallinity and donor polymer aggregation and crystallinity effects on blend microstructures and the resulting optoelectronic performance (**Fig. 9**). Two high-performance polymers, semicrystalline **PTPD3T** and amorphous **PBDTT-FTTE**, were paired with three PDI-based SMAs (**A1–A3**) of differing crystallinity (A1 is the most, A3 is the least crystalline). The resulting TFT and photovoltaic performance trends are strikingly different from typical fullerene-based blends and highly materials-dependent. The present trends reflect synergistic aggregation propensities between the SMA and polymer components. Importantly, the active layer morphology is templated by the PDI in some blends and by the polymer in others, with the latter largely governed by the polymer aggregation/degree of order. Again distinctive “sweet spots” are identified which are planned to analyze with coarse-grain modeling.



**Fig. 9.** The intriguing interplay of small molecule acceptor crystallinity and donor polymer aggregation on the power conversion efficiencies (PCEs) of photoactive blends.

## 2. Design and Realization of New Soft Matter High- $k$ Gate Dielectrics

Under AFOSR support we greatly expanded the available classes of self-assembled high- $k$  nano-dielectrics (SANDs), with each class customized to address a different fabrication challenge (**Fig. 10**). As noted above, the properties of the gate dielectric can profoundly influence the performance characteristics of almost all known TFTs, but especially those fabricated from unconventional semiconductors. The SAND dielectrics are characterized by AFM, conducting AFM, XPS, x-ray reflectivity (XRR), standing wave x-ray reflectivity (SWXRR), x-ray fluorescence (XRF), second harmonic generation (SHG), variable frequency capacitance measurements, TGA, complex impedance spectroscopy, TGA, C-V response of MIM structures, TFT characterization, VUV-radiation hardness measurements (with Dr C. Cress of NRL), and quantum chemical computation (with Prof. M. Ratner). For semiconductors as diverse as organics, sorted carbon nanotubes, single-layer graphene, metal oxide films (amorphous and

polycrystalline) and nanowires, GaAs, and ultra-thin 2-D chalcogenide films, the effects of the SAND gate dielectrics are striking: greatly reduced operating voltage (as much as 50x), greatly enhanced mobility (as much as 3x), and greatly suppressed transfer curve hysteresis arising from trapped charge between the semiconductor and dielectric. Recent work with Ratner has focused on the computational design of SAND building blocks having higher polarizability while blocking charge transport/leakage. We showed that the molecular polarizability, hence the dielectric constant, hence the capacitance can be increased using donor- $\pi$ -bridge-acceptor structures and incorporating polarizable high-Z substituents. We also showed computationally that leakage current through dielectric layers can be greatly suppressed by inserting “quantum interference” structures in the conjugated  $\pi$ -system while at the same time preserving molecular polarizability. In the most recent work, we focused on intermolecular interactions between the  $\pi$ -building blocks in dielectric films. Note that film capacitance scales as the equation,

$$C_i = \frac{k\epsilon_0}{d}$$

where  $k$  = the dielectric constant of the material and  $d$  = the film thickness; it was found in the case of conjugated polyyne building blocks that strong intermolecular interactions lead to a non-linear response of the dielectric constant (Fig. 11), hence the capacitance, which in turn strongly influences the TFT source-drain current and operating voltage. The ultimate goal of this effort is to achieve thin dielectric layers with tunable capacitance and other properties essential for TFT performance.

### 3. Hybrid, Transparent, Flexible Semiconducting Polymer-Amorphous Oxide “Alloys”

This effort grew out of earlier AFOSR-sponsored work on new, low-temperature routes to amorphous, flexible, transparent oxide semiconducting films. A unique combustion-processing technique was developed under AFOSR support to grow flexible, transparent, high-mobility amorphous semiconducting oxide films (essentially heavily crosslinked polymers), suitable for TFT electronics, on polymeric substrates using self-generated internal densification heat from the metal nitrate oxidants and added organic “fuels”. In subsequent work we showed that MO-SAND could be grown directly on amorphous-In-Ga-Zn-O films (a-IGZO) to yield bottom-contact top-gate n-type TFTs with excellent performance (Fig. 12). Note that sputtered polycrystalline IGZO is currently replacing a-silicon in the driving electronics of both LCD (e.g., the iPad Mini, Microsoft Surface 4), and AMOLED (e.g., Samsung Galaxy) displays because of its excellent optical transparency, high TFT mobility, and good current-carrying capacity, which translate into smaller pixel sizes and higher display resolution. In recent work we also showed that we could create patterned a-IGZO features by both high-resolution inkjet printing and by a

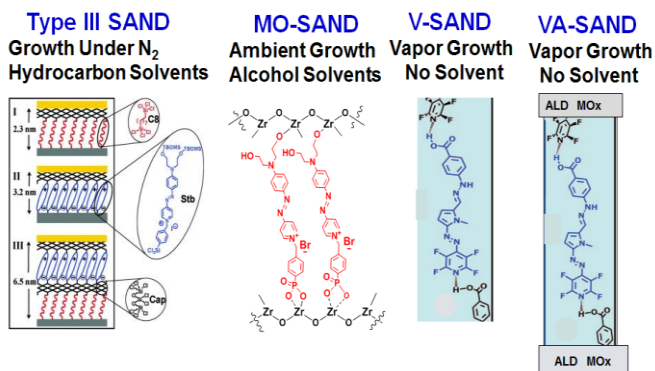


Fig. 10. Classes of self-assembled nanodielectrics (SANDs) created for specific properties and functions.

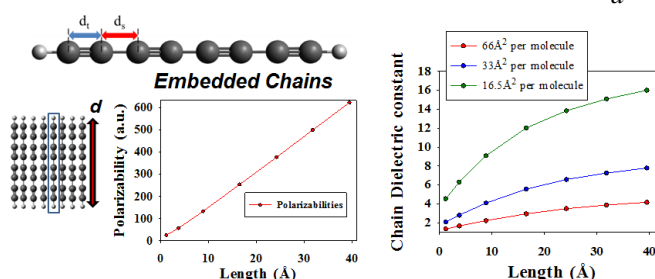
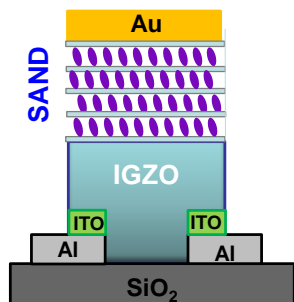


Fig. 11. Packing density effects on the dielectric constants of embedded polyynes of indicated lengths in SAND-type dielectric films.



**Fig. 12.** Bottom contact, top gate combustion-processed a-IGZO TFT with a SAND gate dielectric.  $\mu = 20 \text{ cm}^2/\text{Vs}$ ,  $I_{\text{on}}/I_{\text{off}} = 10^6$ .

spray combustion technique that yields a-IGZO TFTs with electronic metrics comparable to those fabricated by magnetron sputtering. Finally, using spray combustion techniques and appropriate shadow masks, we demonstrated the fabrication of transparent all-oxide (semiconductor, dielectric, and conductor) transistors with excellent TFT metrics (Fig. 13).

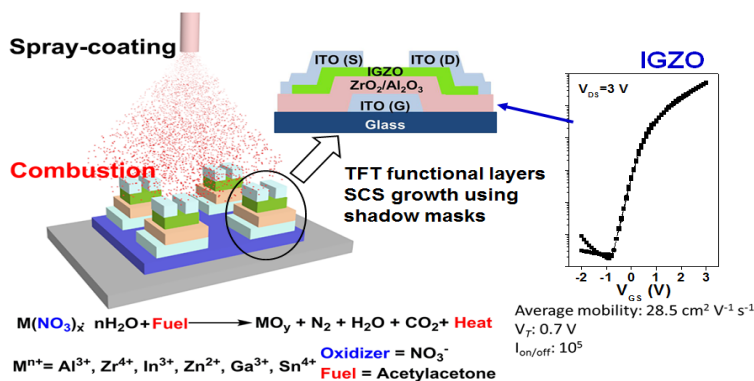
In a second spin-off advance, we showed that polymer-amorphous oxide “alloys” could be fabricated by adding small amounts of water-soluble polymers (e.g., polyvinyl-phenol, polyvinyl alcohol, PEI) to the combustion fuel (Fig. 14). In the case of  $\text{In}_2\text{O}_3 + \text{PVP}$ , the resulting films are optically transparent, mechanically flexible, with  $\mu \approx 10 \text{ cm}^2/\text{Vs}$ , and completely amorphous by XRD. The ramifications of these results and the opportunities they raise will be a topic in the proposed research effort.

### Publications Acknowledging Support by this AFOSR Program

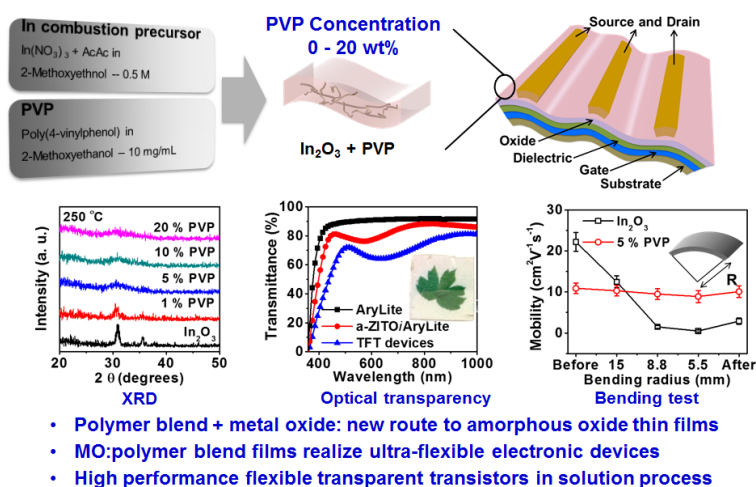
1. Youn, J.; Huang, P.-Y.; Zhang, S.; Liu, C.-W.; Stern, C.; Kim, C.; Chen, M.-C.; Facchetti, A.; Marks, T.J.; Functionalized Benzothieno [3,2-b] thiophenes (BTTs) High Performance Organic Thin-Film Transistors (OTFTs), *J. Mater. Chem. C*. **2014**, 2 (36), 7599-7607. DOI: 10.1039/C4TC01115E.

2. Ha, Y.-G.; Everaerts, K.; Hersam, M.C.; Marks, T.J. Hybrid Gate Dielectric Materials for Unconventional Electronic Circuitry, *Accts. Chem. Res.* **2014**, 47, 1019–1028. DOI: 10.1021/ar4002262

3. Huang, H.; Zhou, N.; Ortiz, R.P.; Chen, Z.; Loser, S.; Zhang, S.; Guo, X.; Casado, J.; Navarrete, J.T.L.; Yu, X.; Facchetti, A.; Marks, T.J. Alkoxy-Functionalized Thienyl-Vinylene Polymers for Field-Effect Transistors and All-Polymer Solar Cells, *Advanced Functional*



**Fig. 13.** All-oxide transparent high-performance a-IGZO transistors fabricated by spray combustion synthesis



**Fig. 14.** Hybrid optically transparent, mechanically flexible, high-mobility polymer-amorphous oxide “alloys”

*Materials*, **2014**, 24, 2782–2793. DOI: 10.1002/adfm.201303219.

4. Riano, A.; Burrezo, P.M.; Mancheno, M.J.; Timalisina, A.; Smith, J.; Facchetti, A.; Marks, T.J.; Navarrete, J.T.L.; Segura, J.L.; Casado, J.; Ponce Ortiz, R.; The unusual electronic structure of ambipolar dicyanovinyl-substituted diketopyrrolopyrrole derivatives, *J. Mater. Chem. C.*, **2014**, 2, 6376–6386. DOI: 10.1039/C4TC00714J.

5. Facchetti, A.; Ortiz, R.P.; Marks, T.J.; Self-Assembled Mono and Multilayers for Functional Opto-Electronic Devices, in *Supramolecular Materials for Opto-Electronics*, Koch, N., Ed. *RSC Smart Materials Series*, **2015**, 119–172. DOI:10.1039/9781782626947.

6. Youn, B.J.; Prabakaran, K.; Emery, J.D.; Leever, B.J.; Kewalramani, S.; Lou, S.J.; Zhang, S.; Lin, Y.-J.; Kim, C.; Chen, P.-S.; Stern, C.; Chang, W.-C.; Bedzyk, M.J.; Chen, L.X.; Chen, M.-C.; Facchetti, A.; Marks, T.J.; Diperfluorophenyl Fused Thiophene Semiconductors for n-Type Organic Thin-Film Transistors (OTFTs), *Advan. Electron. Mater.*, **2015**, 1, 1500098 . DOI: 10.1002/aelm.201500098

7. Yu, X.; Marks, T.J.; Facchetti, A. Metal Oxides for Optoelectronic Applications, *Nature Materials*, **2016**, 15, 383– 396. DOI:10.1038/nmat4599.

8. Zhou, N.; Guo, X.; Ortiz, R.P.; Harschneck, T.; Manley, E.F.; Lou, S.J.; Hartnett, P.E.; Yu, X.; Horowitz, N.E.; Burrezo, P.M.; Aldrich, T.J.; Lopez Navarrete, J.T.; Wasielewski, M.; Chen, L.X.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Marked Consequences of Systematic Oligothiophene Catenation in Thieno[3,4-c]pyrrole-4,6-dione and Bithiopheneimide Photovoltaic Copolymers, *J.Am.Chem. Soc.* **2015**, 137, 12565–12579. DOI: 10.1021/jacs.5b06462.

9. Zhou, N.; Dudnik, A.; Li, T.; Manley, E.F.; Aldrich, T.J.; Guo, P.; Liao, H.C.; Chen, Z.; Chen, L.X.; Chang, R.P.H.; Facchetti, A.; Olvera de la Cruz, O.; Marks, T.J.; All-Polymer Solar Cell Performance Optimized via Systematic Molecular Weight Tuning of Both Donor and Acceptor Polymers, *J.Am.Chem. Soc.* **2016**, 138, 1240–1251. DOI: 10.1021/jacs.5b10735.

10. Guo, X.; Liao, Q.; Manley, E.F.; Wu, Z.; Wang, Y.; Wang, W.; Yang, T.; Shin, Y.-E.; Cheng, X.; Liang, Y.; Chen, L.X.; Baeg, K.-J.; Marks, T.J.; Guo, X.; Materials Design via Optimized Intramolecular Non-Covalent Interactions for High-Performance Organic Semiconductors, *Chemistry of Materials*, **2016**, 28, 2449–2460. DOI: 10.1021/acs.chemmater.6b00850.

11. Takai, A.; Chen, Z.; Yu, X.; Zhou, N.; Marks, T.J.; Facchetti, A.; Annulated Thienyl-Vinylene-Thienyl Building Blocks for Conjugated Copolymers: Ring Dimensions and Isomeric Structure Effects on Conjugation Length and Charge Transport, *Chemistry of Materials*, **2016**, 28, 5772–5783. DOI: 10.1021/acs.chemmater.6b02007.

12. Dudnik, A.S.; Aldrich, T.J.; Eastham, N.D.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Tin-Free Direct C–H Arylation Polymerization for High Photovoltaic Efficiency Conjugated Copolymers, *J. Amer. Chem. Soc.* **2016**, 138,15699–15709. DOI: 10.1021/jacs.6b10023.

13. Eckstein, B.J.; Melkonyan, F.S.; Zhou, N.; Manley, E.F.; Smith, J.; Timalisina, A.; Chang, R.P.H.; Chen, L.X.; Facchetti, A.; Marks, T.J. Buta-1,3-diyne Based  $\pi$ -Conjugated Polymers for Organic Transistors and Solar Cells, *Macromolecules*, **2017**, 50,1430–1441. DOI: 10.1021/acs.macromol.6b02702.

14. Loser, S.; Lou, S.J.; Savoie, B.M.; Bruns, C.J.; Timalisina, A.; Leonardi, M.J.; Harschneck, T.; Turrisi, R.; Zhou, N.; Stern, C.L.; Sarjeant, A.A.; Facchetti, A.; Chang, R.P.H.; Stupp, S.I.;

Ratner, M.A.; Chen, L.X.; Marks, T.J.; Structure-Property Relationships in Heteroacene - Diketopyrrolopyrrole Molecular Donors for Organic Solar Cells, *J. Materials Chem. A*, **2017**, *5*, 9217-9232. DOI: 10.1039/C7TA02037F.

15. Eastham, N.D.; Dudnik, A.S.; Aldrich, T.J.; Manley, E.F.; Fauvell, T.J.; Hartnett, P.E.; Wasielewski, M.R.; Chen, L.X.; Facchetti, A.F.; Chang, R.P.H.; Marks, T.J.; Semiconductor Crystallinity and Donor Polymer Molecular Weight Effects on Templating Film Microstructure and Photovoltaic Performance in Polymer :Perylene Blends, *Chem. Mater.* **2017**, *29*, 4432–4444. DOI: 10.1021/acs.chemmater.7b00964.

16. Huang, W.; Zhuang, X.; Melkonyan, F.S.; Wang, B.; Zeng, L.; Wang, G.; Han, S.; Bedzyk, M.; Yu, J.; Marks, T.J.; Facchetti, A.; UV/Ozone Induced Interfacial Trap Effects in Organic Transistors for High-Sensitivity NO<sub>2</sub> Detection, *Advan. Mater.* **2017**, in press. DOI: 10.1002/adma.201701706.

17. Van Dyck, C.; Marks, T.; Ratner, M.A.; Chain length dependence of the dielectric constant and polarizability in conjugated organic thin films, *ACS Nano*, **2017**, in press. DOI: 10.1021/acsnano.7b01807.

18. Huang, H.; Yang, L.; Facchetti, A.; Marks, T.J.; Molecular and Polymeric Semiconduction Enhanced by Noncovalent Conformational Locks, *Chem. Rev.* **2017**, in press. DOI: 10.1021/acs.chemrev.7b00084.

19. Wang, G.; Huang, W.; Eastham, N.D.; Manley, E.F.; Zeng, L.; Wang, B.; Zhang, X.; Chen, Z.; Li, R.; Melkonyan, F.; Chen, L.X.; Bedzyk, M.J.; Facchetti, A.; Marks, T.J.; Aggregation Control in Shear-Printed Conjugated Polymer Films and Implications for Efficient Charge Transport, *Proc. Nat. Acad. Sci. USA*, **2017**, in press.

20. Wang, G.; Eastham, N.D.; Aldrich, T.J.; Ma, B.; Manley, E.F.; Chen, Z.; Chen, L.X.; Olvera de la Cruz, M.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Photoactive Blend Morphology Engineering through Tunable Aggregation in All-Polymer Solar Cells, **2017**, submitted for publication.

21. Wang, B.; Huang, W.; Marks, T.J.; Facchetti, A.; High-*k* Gate Dielectrics for Emerging Flexible and Stretchable Electronics, **2017**, submitted for publication.

#### **Issued Patents Acknowledging Support by this AFOSR Program**

1. “Low-Temperature Fabrication of Metal Oxide Thin Films and Nanomaterials- Derived Metal Composite Thin Films.” U.S. Patent 8,940,578B2, (2015).

2. “Low-Temperature Fabrication of Metal Oxide Thin Films and Nanomaterials- Derived Metal Composite Thin Films.” U.S. Patent 8,940,579B2, (2015).

3. “Organic-Inorganic Hybrid Multilayer Gate Dielectrics for Thin-Film Transistors.” U.S. Patent No. 9,276,226, (2016).

# AFOSR Deliverables Submission Survey

Response ID:9803 Data

1.

---

**Report Type**

Final Report

---

**Primary Contact Email**

Contact email if there is a problem with the report.

t-marks@northwestern.edu

---

**Primary Contact Phone Number**

Contact phone number if there is a problem with the report

847-491-5658

---

**Organization / Institution name**

Northwestern University

---

**Grant/Contract Title**

The full title of the funded effort.

Polymeric and Molecular Materials for Advanced Organic Electronics

---

**Grant/Contract Number**

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-15-1-0044

---

**Principal Investigator Name**

The full name of the principal investigator on the grant or contract.

Tobin J. Marks

---

**Program Officer**

The AFOSR Program Officer currently assigned to the award

Kenneth C. Caster

---

**Reporting Period Start Date**

03/01/2015

---

**Reporting Period End Date**

02/28/2018

---

**Abstract**

To realize high-performance organic/polymeric/hybrid materials and devices and to address the challenges hindering the progress of printed, flexible, stretchable electronics, it will first be necessary to develop new materials (semiconductors, gate dielectrics, conductive contacts), understand/optimize critical coating/printing processes, study materials interfaces affecting charge injection (contact-semiconductor) and transport (dielectric-semiconductor) as well as to understand/model charge transport and mechanical response in these unconventional devices. Before detailing the proposed research and deliverables, we summarize results from the previous Northwestern (NU) AFOSR-supported program. Significant advances were possible through the highly productive and close collaboration between other NU specialists, other NU faculty, as well as collaborations involving other academic groups (e.g., Stanford U., U. of Illinois Urbana-Champaign, U. of Minnesota, Nat. Central U. of Taiwan, U. of Malaga in Spain, U. Groningen in Holland, Purdue U., U. Cal. Santa Barbara, University College

DISTRIBUTION A: Distribution approved for public release

London, South China U. of Sci. & Tech., and Cambridge U.), national laboratories (Argonne Nat. Lab., AFRL, NIST, NRL), and our nearby industrial transition partners (Polyera Corp., Flexterra Corp.). These collaborations represent a powerful leveraging capability, and involve frequent exchanges of samples and the application of characterization and computational capabilities well beyond any a single research group. At times these interactions capitalize on jointly supervised graduate or postdoctoral students who bring new skills to the AFOSR effort.

In the past effort period major advances were made in the areas outlined below.

1. Organic Semiconductor Synthesis, Characterization, and Processing. Over the past project period, the four central focal points were: i) new ways to manipulate aromatic juncture coplanarity (enhance  $\pi$ -carrier mobility) in semiconducting polymers while maintaining solubility and processability; ii) exploring new  $\pi$ -systems for semi-conducting polymers; iii) exploring new, generalizable, green synthetic routes to semiconducting polymers that avoid large quantities of toxic reagents; iv) realizing the potential of polymer-polymer blends and ternary materials. In focus area i) major progress was made in using strategies that allow some torsional motion to enhance solubility/processability but then "freeze" into coplanarity when the films are solidified. This strategy, "conformational locking" with weak covalent interactions allowed us to create new families of extensively characterized (NMR, X-ray scattering, TGA/DSC, TEM, optical, TFT, SCL transport, OPV, CV, UPS, electronic structure computation) polythiophene donor-acceptor copolymers and to elucidate structure-property relationships. In focus area ii) major progress was made in using diene ( $-C\equiv C-C\equiv C-$ ) linkages to impart combined torsional freedom while maintaining essentially uninterrupted  $\pi$ -delocalization, and offering the intriguing possibility of post-polymerization crosslinking via the diene units. This synthetic strategy yields a family of processable macro-molecules having useful molecular masses, good film-forming characteristics, and extended  $\pi$ -conjugation as judged by optical and opto-electronic metrics. In focus area iii) major progress was made in developing green, environmentally benign synthetic routes to high-performance  $\pi$ -electron polymers can be invented which don't involve classical Stille coupling reactions, hence stoichiometric production of toxic organotin byproducts. A new and highly regioselective direct C-H arylation polymerization (DARP) methodology was developed that enables the reproducible and sustainable synthesis of high-performance  $\pi$ -conjugated semiconducting copolymers. In focus area iv) we asked what advantages polymer-polymer blends might offer in organic electronics; enhancements might include higher charge and exciton mobilities, and greater mechanical, chemical, environmental, and thermal stability. The influence of number-average molecular weight ( $M_n$ ) on the blend film morphology and opto-electronic performance of all-polymer solar cells (APSCs) fabricated with donor polymer PTPD3T and acceptor polymer N2200 (Fig. 8) were systematically investigated. The  $M_n$  effect analysis of both PTPD3T and N2200 was enabled with a modified Carother's equation strategy to produce conjugated polymers with precisely controlled  $M_n$ s. In contrast to reports where maximum power conversion efficiencies (PCEs) are achieved for the highest  $M_n$ s, the present 2-D  $M_n$  optimization matrix strategy locates a "sweet spot" at intermediate  $M_n$ s of both donor and acceptor polymers, a result which is well-explained by the coarse-grain modeling. This study also provides synthetic methodologies to precisely "dial in" conjugated polymers with desired  $M_n$  values and highlights the importance of optimizing  $M_n$  of both components to realize the full potential of blend performance. The reason for this "sweet spot" could be seen in the coarse grain modeling.

## 2. Design and Realization of New Soft Matter High-k Gate Dielectrics

In the past effort period we greatly expanded the available classes of self-assembled high-k nano-dielectrics (SANDs), with each class customized to address a different fabrication challenge. This is important because the properties of the gate dielectric can profoundly influence the performance characteristics of almost all known TFTs, but especially those fabricated from unconventional semiconductors. The SAND dielectrics are characterized by AFM, conducting AFM, XPS, x-ray reflectivity (XRR), standing wave x-ray reflectivity (SWXRR), x-ray fluorescence (XRF), second harmonic generation (SHG), variable frequency capacitance measurements, TGA, complex impedance spectroscopy, TGA, C-V response of MIM structures, TFT characterization, VUV-radiation hardness measurements (with Dr C. Cress of NRL), and quantum chemical computation (with Prof. M. Ratner). For semiconductors as diverse as organics, sorted carbon nanotubes, single-layer graphene, metal oxide films (amorphous and polycrystalline) and nanowires, GaAs, and ultra-thin 2-D chalcogenide films, the effects of the SAND gate dielectrics are striking: greatly reduced operating voltage (as much as 50x), greatly enhanced mobility (as much as 3x), and greatly suppressed transfer curve hysteresis arising from trapped charge between the semiconductor and dielectric. Recent work with Ratner has focused on the computational design of SAND building blocks having higher polarizability while blocking charge transport/leakage. We showed that the molecular polarizability, hence the dielectric constant, hence the capacitance can be increased using donor- $\pi$ -bridge-acceptor structures and incorporating polarizable high-Z substituents.

## 3. Hybrid, Transparent, Flexible Semiconducting Polymer-Amorphous Oxide "Alloys"

This effort grew out of earlier AFOSR-sponsored work on new, low-temperature routes to amorphous, flexible, transparent oxide semiconducting films. A unique combustion-processing technique was developed under AFOSR support to grow

flexible, transparent, high-mobility amorphous semiconducting oxide films (essentially heavily crosslinked polymers), suitable for TFT electronics, on polymeric substrates using self-generated internal densification heat from the metal nitrate oxidants and added organic "fuels". In subsequent work we showed that MO-SAND could be grown directly on amorphous-In-Ga-Zn-O films (a-IGZO) to yield bottom-contact top-gate n-type TFTs with excellent performance. Note that sputtered poly-crystalline IGZO is currently replacing a-silicon in the driving electronics of both LCD (e.g., the iPad Mini, Microsoft Surface 4), and AMOLED (e.g., Samsung Galaxy) displays because of its excellent optical transparency, high TFT mobility, and good current-carrying capacity, which translate into smaller pixel sizes and higher display resolution. In recent work we also showed that we could create patterned a-IGZO features by both high-resolution inkjet printing and by a spray combustion technique that yields a-IGZO TFTs with electronic metrics comparable to those fabricated by magnetron sputtering. In a second spin-off advance, we showed that polymer-amorphous oxide "alloys" could be fabricated by adding small amounts of water-soluble polymers (e.g., polyvinyl-phenol, polyvinyl alcohol, PEI) to the combustion fuel. In the case of In<sub>2</sub>O<sub>3</sub> + PVP, the resulting films are optically transparent, mechanically flexible, with  $\mu \approx 10$  cm<sup>2</sup>/Vs, and completely amorphous by XRD. The ramifications of these results and the opportunities they raise will be a topic of future research.

---

### Distribution Statement

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

---

### Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

---

### SF298 Form

Please attach your SF298 form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[sf0298AFOSR.pdf](#)

---

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

[AFOSRfinalreport052018tmRev.pdf](#)

---

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

---

### Archival Publications (published) during reporting period:

1. Youn, J.; Huang, P.-Y.; Zhang, S.; Liu, C.-W.; Stern, C.; Kim, C.; Chen, M.-C.; Facchetti, A.; Marks, T.J.; Functionalized Benzothieno [3,2-b] thiphenes (BTTs) High Performance Organic Thin-Film Transistors (OTFTs), *J. Mater. Chem. C.* 2014, 2 (36), 7599-7607.  
DOI: 10.1039/C4TC01115E.
2. Ha, Y.-G.; Everaerts, K.; Hersam, M.C.; Marks, T.J. Hybrid Gate Dielectric Materials for Unconventional Electronic Circuitry, *Accts. Chem. Res.* 2014, 47, 1019–1028.  
DOI: 10.1021/ar4002262
3. Huang, H.; Zhou, N.; Ortiz, R.P.; Chen, Z.; Loser, S.; Zhang, S.; Guo, X.; Casado, J.; Navarrete, J.T.L.; Yu, X.; Facchetti, A.; Marks, T.J. Alkoxy-Functionalized Thienyl-Vinylene Polymers for Field-Effect Transistors and All-Polymer Solar Cells, *Advanced Functional Materials*, 2014, 24, 2782–2793. DOI: 10.1002/adfm.201303219.
4. Riano, A.; Burrezo, P.M.; Mancheno, M.J.; Timalina, A.; Smith, J.; Facchetti, A.; Marks, T.J.; Navarrete, J.T.L.; Segura, J.L.; Casado, J.; Ponce Ortiz, R.; The unusual electronic structure of ambipolar dicyanovinyl-substituted diketopyrrolopyrrole derivatives, *J. Mater. Chem. C.*, 2014, 2, 6376-6386. DOI: 10.1039/C4TC00714J.
5. Facchetti, A.; Ortiz, R.P.; Marks, T.J.; Self-Assembled Mono and Multilayers for Functional Opto-Electronic Devices, in  
DISTRIBUTION A: Distribution approved for public release

Supramolecular Materials for Opto-Electronics, Koch, N., Ed. RSC Smart Materials Series, 2015, 119-172.

DOI:10.1039/9781782626947.

6. Youn, B.J.; Prabakaran, K.; Emery, J.D.; Leever, B.J.; Kewalramani, S.; Lou, S.J.; Zhang, S.; Lin, Y.-J.; Kim, C.; Chen, P.-S.; Stern, C.; Chang, W.-C.; Bedzyk, M.J.; Chen, L.X.; Chen, M.-C.; Facchetti, A.; Marks, T.J.; Diperfluorophenyl Fused Thiophene Semiconductors for n-Type Organic Thin-Film Transistors (OTFTs), *Advan. Electron. Mater.*, 2015, 1, 1500098. DOI: 10.1002/aelm.201500098

7. Yu, X.; Marks, T.J.; Facchetti, A. Metal Oxides for Optoelectronic Applications, *Nature Materials*, 2016, 15, 383- 396. DOI:10.1038/nmat4599.

8. Zhou, N.; Guo, X.; Ortiz, R.P.; Harschneck, T.; Manley, E.F.; Lou, S.J.; Hartnett, P.E.; Yu, X.; Horowitz, N.E.; Burrezo, P.M.; Aldrich, T.J.; Lopez Navarrette, J.T.; Wasielewski, M.; Chen, L.X.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Marked Consequences of Systematic Oligothiophene Catenation in Thieno[3,4-c]pyrrole-4,6-dione and Bithiopheneimide Photovoltaic Copolymers, *J.Am.Chem. Soc.* 2015, 137, 12565–12579. DOI: 10.1021/jacs.5b06462.

9. Zhou, N.; Dudnik, A.; Li, T.; Manley, E.F.; Aldrich, T.J.; Guo, P.; Liao, H.C.; Chen, Z.; Chen, L.X.; Chang, R.P.H.; Facchetti, A.; Olvera de la Cruz, O.; Marks, T.J.; All-Polymer Solar Cell Performance Optimized via Systematic Molecular Weight Tuning of Both Donor and Acceptor Polymers, *J.Am.Chem. Soc.* 2016, 138, 1240–1251. DOI: 10.1021/jacs.5b10735.

10. Guo, X.; Liao, Q.; Manley, E.F.; Wu, Z.; Wang, Y.; Wang, W.; Yang, T.; Shin, Y.-E.; Cheng, X.; Liang, Y.; Chen, L.X.; Baeg, K.-J.; Marks, T.J.; Guo, X.; Materials Design via Optimized Intramolecular Non-Covalent Interactions for High-Performance Organic Semiconductors, *Chemistry of Materials*, 2016, 28, 2449–2460. DOI: 10.1021/acs.chemmater.6b00850.

11. Takai, A.; Chen, Z.; Yu, X.; Zhou, N.; Marks, T.J.; Facchetti, A.; Annulated Thienyl-Vinylene-Thienyl Building Blocks for Conjugated Copolymers: Ring Dimensions and Isomeric Structure Effects on Conjugation Length and Charge Transport, *Chemistry of Materials*, 2016, 28, 5772–5783. DOI: 10.1021/acs.chemmater.6b02007.

12. Dudnik, A.S.; Aldrich, T.J.; Eastham, N.D.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Tin-Free Direct C–H Arylation Polymerization for High Photovoltaic Efficiency Conjugated Copolymers, *J. Amer. Chem. Soc.* 2016, 138, 15699–15709. DOI: 10.1021/jacs.6b10023.

13. Eckstein, B.J.; Melkonyan, F.S.; Zhou, N.; Manley, E.F.; Smith, J.; Timalisina, A.; Chang, R.P.H.; Chen, L.X.; Facchetti, A.; Marks, T.J. Buta-1,3-diyne Based  $\pi$ -Conjugated Polymers for Organic Transistors and Solar Cells, *Macromolecules*, 2017, 50, 1430–1441.

DOI: 10.1021/acs.macromol.6b02702.

14. Loser, S.; Lou, S.J.; Savoie, B.M.; Bruns, C.J.; Timalisina, A.; Leonardi, M.J.; Harschneck, T.; Turrisi, R.; Zhou, N.; Stern, C.L.; Sarjeant, A.A.; Facchetti, A.; Chang, R.P.H.; Stupp, S.I.; Ratner, M.A.; Chen, L.X.; Marks, T.J.; Structure-Property Relationships in Heteroacene - Diketopyrrolopyrrole Molecular Donors for Organic Solar Cells, *J. Materials Chem. A*, 2017, 5, 9217-9232. DOI: 10.1039/C7TA02037F.

15. Eastham, N.D.; Dudnik, A.S.; Aldrich, T.J.; Manley, E.F.; Fauvell, T.J.; Hartnett, P.E.; Wasielewski, M.R.; Chen, L.X.; Facchetti, A.F.; Chang, R.P.H.; Marks, T.J.; Semiconductor Crystallinity and Donor Polymer Molecular Weight Effects on Templating Film Microstructure and Photovoltaic Performance in Polymer :Perylene Blends, *Chem. Mater.* 2017, 29, 4432–4444. DOI: 10.1021/acs.chemmater.7b00964.

16. Huang, W.; Zhuang, X.; Melkonyan, F.S.; Wang, B.; Zeng, L.; Wang, G.; Han, S.; Bedzyk, M.; Yu, J.; Marks, T.J.; Facchetti, A.; UV/Ozone Induced Interfacial Trap Effects in Organic Transistors for High-Sensitivity NO<sub>2</sub> Detection, *Advan. Mater.* 2017, in press. DOI: 10.1002/adma.201701706.

17. Van Dyck, C.; Marks, T.; Ratner, M.A.; Chain length dependence of the dielectric constant and polarizability in conjugated organic thin films, *ACS Nano*, 2017, in press.

DOI: 10.1021/acsnano.7b01807.

18. Huang, H.; Yang, L.; Facchetti, A.; Marks, T.J.; Molecular and Polymeric Semiconduction Enhanced by Noncovalent Conformational Locks, *Chem. Rev.* 2017, in press. DOI: 10.1021/acs.chemrev.7b00084.

19. Wang, G.; Huang, W.; Eastham, N.D.; Manley, E.F.; Zeng, L.; Wang, B.; Zhang, X.; Chen, Z.; Li, R.; Melkonyan, F.; Chen, L.X.; Bedzyk, M.J.; Facchetti, A.; Marks, T.J.; Aggregation Control in Shear-Printed Conjugated Polymer Films and Implications for Efficient Charge Transport, *Proc. Nat. Acad. Sci. USA*, 2017, in press.

20. Wang, G.; Eastham, N.D.; Aldrich, T.J.; Ma, B.; Manley, E.F.; Chen, Z.; Chen, L.X.; Olvera de la Cruz, M.; Chang, R.P.H.; Facchetti, A.; Marks, T.J.; Photoactive Blend Morphology Engineering through Tunable Aggregation in All-Polymer Solar Cells, 2017, submitted for publication.

21. Wang, B.; Huang, W.; Marks, T.J.; Facchetti, A.; High-k Gate Dielectrics for Emerging Flexible and Stretchable Electronics, 2017, submitted for publication

**New discoveries, inventions, or patent disclosures:**

**Do you have any discoveries, inventions, or patent disclosures to report for this period?**

Yes

**Please describe and include any notable dates**

Issued Patents Acknowledging Support by this AFOSR Program

- 1."Low-Temperature Fabrication of Metal Oxide Thin Films and Nanomaterials- Derived Metal Composite Thin Films." U.S. Patent 8,940,578B2, (2015).
- 2."Low-Temperature Fabrication of Metal Oxide Thin Films and Nanomaterials- Derived Metal Composite Thin Films." U.S. Patent 8,940,579B2, (2015).
- 3."Organic-Inorganic Hybrid Multilayer Gate Dielectrics for Thin-Film Transistors." U.S. Patent No. 9,276,226, (2016).

**Do you plan to pursue a claim for personal or organizational intellectual property?**

Yes

**Changes in research objectives (if any):**

None

**Change in AFOSR Program Officer, if any:**

Charles Lee retired and was replaced by Kenneth Caster

**Extensions granted or milestones slipped, if any:**

None

**AFOSR LRIR Number**

**LRIR Title**

**Reporting Period**

**Laboratory Task Manager**

**Program Officer**

**Research Objectives**

**Technical Summary**

**Funding Summary by Cost Category (by FY, \$K)**

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

**Report Document**

**Report Document - Text Analysis**

---

**Report Document - Text Analysis**

---

**Appendix Documents**

---

## 2. Thank You

---

### **E-mail user**

May 20, 2018 12:51:55 Success: Email Sent to: t-marks@northwestern.edu

---