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Modular Conjugated Polymers for Mid-Infrared Photonic Applications

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14. ABSTRACT <p>Over the course of the project related to the development of conjugated polymers for optical to electrical signal transduction of infrared (IR) light we have made significant strides in many of the originally-proposed research areas. Namely, we have: (1) continued to demonstrate the capability to systematically and precisely control the properties of donor-acceptor (DA) conjugated polymers (CPs) extending throughout the short-, mid-wavelength infrared (MWIR: 1.4–8 μm) and long-wavelength infrared (LWIR: 8–14 μm); (2) demonstrated improvements in the capability to control the electronic structure of narrow bandgap conjugated polymers leading to the discovery of new phenomena and functionality from organic materials; (3) developed new materials and devices enabling the first examples of photodetection from the SWIR–LWIR using organic materials; and (4) demonstrated high performance photoconductive devices that outperform their inorganic counterparts through collaborative efforts with AFRL. Thus, we have been able to advance the design of organic semiconductors (OSCs) enabling new classes of materials, new (opto)electronic and physical functionality, and new device technologies. Moreover, funding of this work by the AFOSR has allowed our team to become a world leader in the chemistry, photophysics, and solid-state device applications of narrow bandgap and open-shell CPs and organic infrared optoelectronics. We have continued to make additional significant discoveries in narrow bandgap materials such as ground state electronics that can be manipulated, conductivities that are higher than other neutral organic solids and demonstrate unique electrical, optical, spin, thermal, magnetic, and quantum phenomena.</p>					
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Lead Organization: University of Southern Mississippi

Technical Point of Contact: Professor Jason D. Azoulay

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Proposal Title

Modular Conjugated Polymers for Mid-Infrared Photonic Applications

AFOSR Program Manager: Dr. Kenneth Caster

Executive Summary of Research Accomplishments and Technical Achievements

Over the course of the project related to the development of conjugated polymers for optical to electrical signal transduction of infrared (IR) light we have made significant strides in many of the originally-proposed research areas. Namely, we have: (1) continued to demonstrate the capability to systematically and precisely control the properties of donor-acceptor (DA) conjugated polymers (CPs) extending throughout the short-, mid-wavelength infrared (MWIR: 1.4–8 μm) and long-wavelength infrared (LWIR: 8–14 μm); (2) demonstrated improvements in the capability to control the electronic structure of narrow bandgap conjugated polymers leading to the discovery of new phenomena and functionality from organic materials; (3) developed new materials and devices enabling the first examples of photodetection from the SWIR–LWIR using organic materials; and (4) demonstrated high performance photoconductive devices that outperform their inorganic counterparts through collaborative efforts with AFRL.

Thus, we have been able to advance the design of organic semiconductors (OSCs) enabling new classes of materials, new (opto)electronic and physical functionality, and new device technologies. Moreover, funding of this work by the AFOSR has allowed our team to become a world leader in the chemistry, photophysics, and solid-state device applications of narrow bandgap and open-shell CPs and organic infrared optoelectronics. We have continued to make additional significant discoveries in narrow bandgap materials such as ground state electronics that can be manipulated, conductivities that are higher than other neutral organic solids and demonstrate unique electrical, optical, spin, thermal, magnetic, and quantum phenomena. This would not have been possible without AFOSR support, and we thank the agency greatly for this opportunity to improve the chemistry and physics of organic electronic materials such that these technologies can be translated to the warfighter while simultaneously advancing the scientific knowledge of the United States. Specifically, we have addressed the following major technical objectives over the course of the project:

1. Developed synthetic approaches that allow for control over the frontier orbital energetics (separation, position, and alignment), ground state electronics, interchain arrangements, solid-state properties, and many other molecular features with a higher degree of synthetic precision than previously demonstrated. This has resulted in the unique in the world capability to systematically control the properties of these materials in the IR

spectral regions and develop charge neutral conjugated polymers (CPs) with the lowest energy excitations reported.

2. Demonstrated organic-based IR devices that are responsive from the visible to the long-wavelength infrared and which operate at room temperature.
3. Further elucidated fundamental properties associated with charge photogeneration in these devices. Demonstrated that while there are challenges with recombination losses and increasing thermal generation noise, that controlling materials structure, film disorder, and new device structures can lead to promising improvements and performance comparable to or exceeding their inorganic counterparts.
4. Demonstrated molecular design guidelines which address and to some extent overcome considerations noted in Point 3. For organic photodiodes (OPDs), these include identification of chemical modifications that increase exciton dissociation efficiency such as various chemical substitution patterns or modifying the dielectric of the film. Collectively, these fundamental studies have allowed us to delineate structure-function-property relationships and rationally improve performance. Significant improvements are anticipated considering these results.
5. Through collaborative efforts, demonstrated new technologies based on polymer photodiodes that operate in the IR. Provided demonstrations of spectroscopic analysis, image reconstruction, health and medical monitoring, and OPDs for imaging applications.
6. Developed the fundamental chemistry enabling the development of charge neutral π -conjugated macromolecular chemistries with narrow bandgaps, strong electronic correlations, and tunable open-shell configurations with electronic states that span the entire range from “conventional” closed-shell structures, to biradicaloids ($0 < y < 1$) with varying amounts of open-shell character, to diradicals ($y = 1$) in both singlet ($S = 0$) and triplet ($S = 1$) spin states with varying energetics. These materials open access to a broad variety of technologically relevant applications once thought of as beyond the current scope of organic semiconductors.
7. Demonstrated photoconductive polymer detectors utilizing a donor–acceptor conjugated polymer with broadband operation from the short- to long-wave infrared. Room-temperature detectivities are comparable to lead salts and closely approach those of cooled, state-of-the-art epitaxial devices based on InGaAs, InSb, and HgCdTe, providing a fundamentally new platform for broadly applicable, low cost, ambient temperature infrared optoelectronics.
8. Visited Air Force Research Labs Materials and Manufacturing Directorate (AFRL/RX) and Sensors Directorate (AFRL/RY) on multiple occasions and established collaborations. A diversity of materials have been synthesized and devices fabricated which have been transferred to AFRL researchers. These are the focus of ongoing collaborative efforts.

9. Hosted visitors from AFRL on 9/9 – 9/11/19 including: Dr. Chris Brewer – Branch Chief, Photonic Materials Branch, Dr. Tod Grusenmeyer – Research Chemist, Functional Materials Division, Dr. Jarret Vella – Research Chemist, Electro-Optics/Infrared Components Branch, and Dr. John Derov – Physicist, Sensors Directorate. White papers were drafted based on AFRL needs and strategic directions, with programmatic efforts underway.
10. Established A CRADA between USM and AFRL/RV. Efforts related to the development of IR and other technologies are ongoing between USM and AFRL/RV. A provisional patent application (joint invention between AFRL and USM) has been filed (6/2020). Manuscripts between AFRL and USM have been submitted.
11. Funded multiple new projects utilizing new materials concepts and fundamental discoveries emanating from AFOSR funding.

Accomplishing the above objectives has resulted in tangible metrics for this project in terms of the education of graduate students, undergraduate participants, dissemination of results, and recognition for our work. In particular, the support of the AFOSR has allowed the following events to occur.

1. Three graduate students and two undergraduate students were fully or partially supported on this project, with one graduate student recently completing their Ph.D. The ability to provide the stipend, benefits, tuition, and materials/supplies has proven invaluable to the continued success of the laboratory.
2. Ten manuscripts have been published (two submitted) over the course of the award. One patent application has been filed and another submitted. Furthermore, many additional manuscripts/patents are being prepared by our team and collaborators. The published manuscripts and patent applications are detailed below.

Year 3: (July 1, 2019 – September 30, 2020)

- a. M. Steelman, D. J. Adams, K. Mayer, M. Lockart, L. Galuska, P. Mahalingam, M. Saghayezhian, X. Gu, M. K. Bowman, J. D. Azoulay “Magnetic Ordering in a High-Spin Donor–Acceptor Conjugated Polymer” *Submitted*.
- b. J. Vella, L. Huang, N. Eedugurala, K. M. Mayer, T. N. Ng., J. D. Azoulay “Broadband Infrared Photodetection Using a Narrow Bandgap Conjugated Polymer” *Submitted*.
- c. J. Vella, M. I. Vakil, L. Huang, N. Eedugurala, J. D. Azoulay “Infrared Detection with Intrinsically Conductive Conjugated Polymers” USM Disclosure No. 2020.0026, **2020**.
- d. Li, J. Lim, J. D. Azoulay, D. Leem, and T.N. Ng “Tuning the charge blocking layer to enhance photomultiplication in organic shortwave infrared photodetectors” *J. Mater. Chem. C*, **2020**, Advance Article. doi.org/10.1039/D0TC03013A

- e. Z. Wu, N. Li, N. Eedugurala, J. D. Azoulay, D. S. Leem, T. N. Ng. “Noise and detectivity limits in organic shortwave infrared photodiodes with low disorder” *npj Flex. Electron* 4, 6 (2020).
- f. H. Kim, Z. Wu, N. Eedugurala, J. D. Azoulay, T. N. Ng, “Solution-Processed Phototransistors Combining Organic Absorber and Charge Transporting Oxide for Visible to Infrared Light Detection” *ACS Appl. Mater. Interfaces* **2019**, 11, 40, 36880 – 36885.
- g. K. Wang, L. Huang, N. Eedugurala, S. Zhang, Md A. Sabuj, N. Rai, X. Gu, J. D. Azoulay, T. N. Ng “Wide Potential Window Supercapacitors Using Open-Shell Donor-Acceptor Conjugated Polymers with Stable N-doped States” *Adv. Energy Mater.* **2019**, 1902806.

Year 1–2: (July 1, 2017 – July 1, 2019)

- h. J. D. Azoulay, L. Huang, N. Edegurula, A. E. London “Open-Shell Conjugated Polymer Conductors, Composites and Compositions” PCT/US19/30950, **2019**.
 - i. W. Yao, Z. Wu, E. Huang, L. Huang, A. E. London, Z. Liu, J. D. Azoulay, T. N. Ng “Organic Bulk Heterojunction Infrared Photodiodes for Imaging Out to 1300 nm” *ACS Appl. Elec. Mater.*, **2019**, 15, 660-666.
 - j. Z. Wu, Y. Zhai, H. Kim, J. D. Azoulay, T. N. Ng “Emerging Design and Characterization Guidelines for Polymer-Based Infrared Photodetectors” *Acc. Chem. Res.* **2018**, 51, 3144–3153.
 - k. Y. Joo, L. Huang, N. Eedugurala, A. E. London, A. Kumar, B. M. Wong, B. W. Boudouris, and J. D. Azoulay "Enhancing the Thermoelectric Performance of an Open-Shell Donor-Acceptor Conjugated Polymer by Doping with a Radical-Containing Small Molecule" *Macromolecules*, **2018**, 51(10), 3886–3894.
 - l. Z. Wu, W. Yao, A. E. London, J. D. Azoulay, Tse Nga Ng "Elucidating the Detectivity Limits in Shortwave Infrared Organic Photodiodes" *Adv. Functional Materials*, **2018**, 28(18), 1800391.
 - m. D. B. Sulas, A. E. London, L. Huang, L. Xu, Z. Wu, T. N. Ng, B.M. Wong, C. W. Schlenker, J. D. Azoulay, M. Y. Sfeir "Preferential Charge Generation at Aggregate Sites in Narrow Band Gap Infrared Photoresponsive Polymer Semiconductors" *Adv. Optical Materials*, **2018**, 6(7), 1701138.
 - n. L. Huang, A. E. London, B. A. Zhang, M. B. Oviedo, J. Tropp, W. Yao, Z. Wu, B. M. Wong, T. N. Ng, J. D. Azoulay “Donor–Acceptor Polymers with Tunable Infrared Photoresponse” *Polymer Chemistry*, **2017**, 8(19), 2922-2930. **(Highlighted on Back Cover).**
3. In addition to these tangible products, the AFOSR-supported work has also brought significant recognition and resources to the group. We have further translated our research directions on the development in IR optoelectronics and narrow bandgap materials with open-shell electronic structures into a state-wide program and provided leadership in the state’s infrastructure improvement grant from NSF entitled “Center for Emergent Molecular Optoelectronics (CEMOs)” awarded for \$20 million in late 2018. This center is currently establishing an interdisciplinary multi-institution materials research program between the four MS research universities directed at critical and contemporary optoelectronic and energy challenges in key focus areas of fundamental

science and engineering research and education. In 2018, Azoulay built a state-of-the-art facility which has helped SPSE to attract new faculty, additional funding, house regionally distinct advanced materials characterization and device fabrication, engineering, and testing equipment. Grants and facilities of this nature are enabling SPSE to conduct transformative research in new areas previously unavailable within the university and the state, educate and train future polymer scientists, and fortify the University's reputation as a global leader in polymer science. Polymergent, a spin-off company was started by Azoulay to commercialize discoveries and materials based on narrow bandgap and infrared polymers. Clearly, none of this would have been possible without the initial investment by AFOSR and support of Dr. Caster and the AFOSR team.

Detailed Research Results

Introduction

Inorganic semiconductors, complex manufacturing systems, and specialized fabrication facilities are the basis for IR optoelectronics. Current technology remains largely dependent on epitaxially grown, lattice-matched, crystalline devices, which suffer from limited modularity, intrinsic fragility, low speed, high-power consumption, require cryogenic cooling, and are largely incompatible with Si CMOS processes. The inexorable growth of applications, new areas, and demands on components will outpace the capabilities offered by current materials and devices. Unlike inorganics, photoexcitation of organic semiconductors (OSCs) results in bound electron-hole pairs (excitons), which require a suitable energy offset, facilitated by a higher electron affinity acceptor, to separate the exciton and drive charge transfer. Dissociated charges are transported to their respective electrodes through interpenetrating bicontinuous donor and acceptor networks formed through nanoscale phase separation. While general design guidelines exist to tailor the HOMO-LUMO (highest occupied/lowest unoccupied molecular orbital) energies, absorption profiles, and transport characteristics of OSCs, the complex interrelation between electronic properties and conformational disorder has precluded similar control in the IR. Detection in the information rich NIR–SWIR–MWIR–LWIR spectral regions can therefore only be achieved using conventional solid-state inorganic materials systems.

The originally stated goals of the proposal, which have been exceeded are listed below:

- Develop robust synthetic methodologies to access narrow band gap DA conjugated copolymers.
- Investigate how intramolecular π -delocalization, intramolecular charge-transfer characteristics, geometric structure, various functionality, frontier orbital energetics, and intermolecular interactions influence the properties of these materials in a systematic and controlled fashion.
- Generate modular materials with effective and controlled spectral coverage in the short-wavelength IR (SWIR: 1.4–3 μm), and extending into the MWIR (> 3 μm) with properties suitable for detecting long-wavelength light.
- Investigate more complex conjugation pathways for the generation of broadband absorbers and extending absorption.
- Investigate optical to electrical signal transduction of long-wavelength light, primarily in the 2–5 μm region.

- Establish design rules for further guiding experiments, materials development, and for rationally predicting properties.
- Develop an understanding of the molecular requirements for efficient photo-driven electron/hole transport within these systems.
- Investigate the range, sensitivity, detectivity, dark resistance, and response speeds of new photoconductive materials with very narrow band gaps and compare them to archetypal systems such as PbSe (1.5–5.2 μm), and alloys of HgCdTe currently employed in the SWIR–MWIR.
- Evaluate new IR device applications, light sensing modalities, and hybrid organic-inorganic nanocomposites.
- Collaborate with leaders in academia, industry, and at national laboratories with expertise in advanced optical spectroscopy, quantum chemical methods, and device fabrication and engineering to assess the *functionality* of these new materials.

Research supported through AFOSR has enabled us to establish leadership in the synthesis, development, and application of narrow bandgap CPs and related materials affording: i) precision synthetic methods that afford insight into complex structure-property-performance relationships; ii) bandgap control at very low energies (1.0 \rightarrow \sim 0.1 eV, Fig. 1); iii) the development of strategies to enable an IR photoresponse; and iv) control of the electronic structure to enable new properties not previously measured in soft-matter systems. This has provided a means to undertake significant investigations at the interface of disciplines and enabled fresh approaches towards the development of new technologies as summarized below.

I. Synthesis of Narrow Bandgap DA CPs

Incorporation of peripheral cross-conjugated substituents within a π -conjugated system provides a versatile and highly valuable tool for tuning the properties of CPs. This affords systematic and precise control of the properties in the Vis and IR (Fig. 1). Through a study of > 300 donor-acceptor (DA) CPs, we demonstrated, with experimental verification, the ability of computational approaches to provide *reliable trends* in the evolution of the HOMO-LUMO energies and optical gaps. Figure 1 depicts a subset of these materials, consistent with the capability to access highly modular materials, with a variety of molecular configurations, spanning the NIR

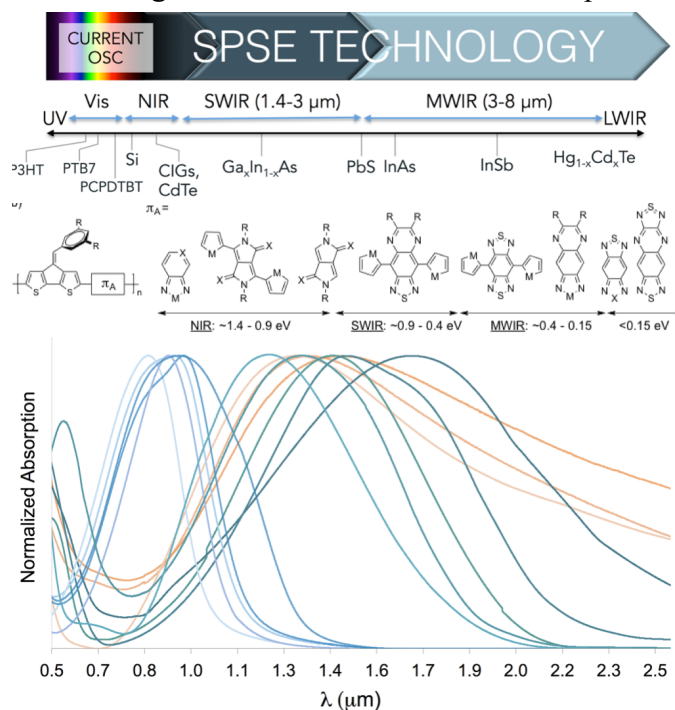


Figure 1. (Top) Traditional range of CPs and inorganics for light detection. (Middle) Various heterocycles in combination with bridgehead olefin cyclopentadithiophene (CPDT) donor. (Bottom) Examples of CPs synthesized spanning the NIR-SWIR and extending into the MWIR-LWIR.

(0.9–1.4 μm), SWIR (1.4–3 μm), and even MWIR–LWIR (3–14 μm). From these efforts we identified general design guidelines that will allow the discovery of a broader class of narrow bandgap materials: 1) collinear conjugated units with minimal torsion-susceptible linkages which preserve the electronic structure; 2) side-chain substitution that does not introduce pervasive backbone torsion; 3) strong intramolecular electronic interactions; 4) modular frameworks amenable to precise changes; and 5) local alterations of aromatic character within units fused or cross-conjugated to the main chain. Thus, we are able to control the properties of diverse materials sets in the proposed spectral regions – a unique in the world capability.

II. Infrared Organic Optoelectronics.

We have demonstrated *the first* example of control of the properties of CPs in the infrared (IR) spectral regions from $0.9 < \lambda < 14 \mu\text{m}$. Building on this expertise, we developed new materials, soft matter systems, and device paradigms enabling optical to electrical transduction of IR light. Photodiodes show a response to $\sim 2.0 \mu\text{m}$, while photoconductors respond across the SWIR–LWIR, demonstrating the longest wavelength light detected using CPs and organic materials outside of graphene.

For photodiodes leveraging excitonic processes, we discovered that charge generation assisted by polymer aggregation and coherent phenomena are essential to compensate for the energy gap law, which dictates that excited state lifetimes decrease as the bandgap narrows (*Adv. Optical Materials*, **2018**, 6(7), 1701138). Fundamental investigations of polymer and device physics have resulted in improving performance to levels now matching commercial inorganic photodiodes (*ACS Appl. Mater. Interfaces* **2019**, 11, 40, 36880 – 36885). We demonstrated a high level of gain using trap-assisted photomultiplication mechanisms enabling significant enhancements in the sensitivity of organic photodiodes (*J. Mater. Chem. C*, **2020**, doi: 10.1039/D0TC03013A). We have integrated these photodetectors within a wide range of systems such as wearable physiological monitors and SWIR spectroscopic imagers that enable compositional analysis for food, water quality monitoring, imaging, and medical and biological studies (*ACS Appl. Elec. Mater.*, **2019**, 1(5), 660 – 666; previous efforts: *Acc. Chem. Res.* **2018**, 51, 3144–3153). More recent unpublished work demonstrates additional imaging demonstrations such as object inspection, imaging through smog, and recording of blood vessel location and flow. Newly developed photoconductive detectors outperform their inorganic counterparts and operate at room temperature with high response speeds. These materials and devices are the focus of efforts with research groups around the world, through a cooperative research and development agreement (CRADA) with AFRL/RY Electro-Optics/Infrared Components Branch, and industrial partners. These studies are also providing a fundamental understanding of how organic molecules interact with IR light and are the first of their kind that detail general design rules for incorporating CPs into high performing IR optoelectronics, articulate specific challenges associated with these materials, and that connect intrinsic properties with device performance. *Past efforts discussed in previous reports and details related to work that has not been protected by a patent application or published are omitted. An emphasis on Year 3 findings is discussed below.*

Solution-Processed Phototransistors

We demonstrated a high-performance infrared phototransistor that uses a broad-band absorbing organic bulk heterojunction (BHJ) layer responsive from the visible to the shortwave infrared (SWIR), from 500 to 1400 nm. The device structure is based on a bilayer transistor

channel that decouples charge photogeneration and transport, enabling independent optimization of each process. The organic BHJ layer is improved by incorporating camphor, a highly polarizable additive that increases carrier lifetime. An indium zinc oxide transport layer with high electron mobility is employed for rapid charge transport. As a result, the phototransistors achieve a dynamic range of 127 dB and reach a specific detectivity of 5×10^{12} Jones under a low power illumination of 20 nW/cm^2 , outperforming commercial germanium photodiodes in the spectral range below 1300 nm . The photodetector metrics are measured with respect to the applied voltage, incident light power, and temporal bandwidth, demonstrating operation at a video-frame rate of 50 Hz .

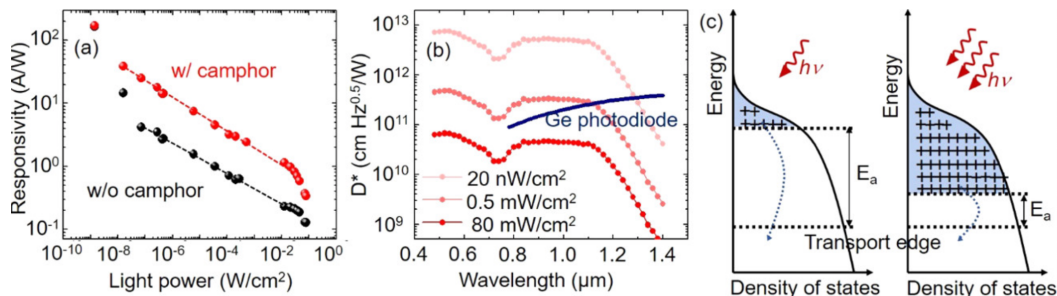


Figure 2. (a) Responsivity and (b) detectivity as a function of incident light power. The phototransistor with camphor (data in red) is biased at $V_{GS} = -10 \text{ V}$, $V_{DS} = 5 \text{ V}$, and the light source is modulated at 10 Hz from an LED at a 940 nm wavelength. The blue line indicates commercial germanium photodiode. (c) Schematic diagram of trap occupancy under different light power.

In collaboration with Tina Ng at UCSD we developed materials and high-performance infrared photodiodes and phototransistors using broadband absorbing organic bulk heterojunction (BHJ) layer responsive from 500 nm to 1800 nm . To achieve high detectivity in IR detectors, it is critical to reduce the device noise. However, for non-crystalline semiconductors, an essential framework is missing to understand and predict the effects of disorder on the dark current. We recently reported experimental and modeling studies on the noise current in exemplar organic bulk heterojunction photodiodes, with 10 donor–acceptor combinations spanning wavelengths between 800 and 1600 nm (*npj Flexible Electronics*, **6**, **2020**). A significant reduction of the noise and higher detectivity were found in devices using non-fullerene acceptors (NFAs) in comparison to those using fullerene derivatives. The low noise in NFA blends was attributed to a sharp drop off in the distribution of bandtail states, as revealed by variable-temperature density-of-states measurements. Taking disorder into account, we developed a general physical model to explain the dependence of thermal noise on the effective bandgap and bandtail spread. The model provides theoretical targets for the maximum detectivity that can be obtained at different detection wavelengths in inherently disordered infrared photodiodes.

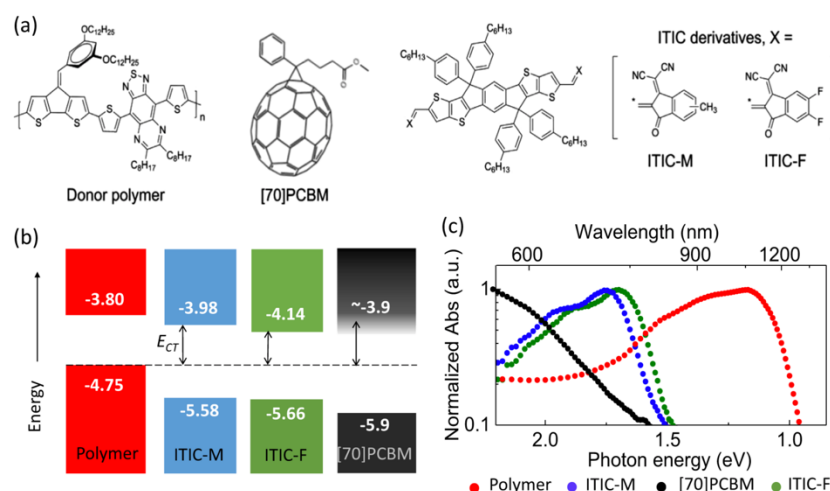


Figure 3. Chemical structure and energy levels of IR donor-acceptor polymer with respect to different acceptors. Normalized absorption spectra for pristine organic semiconductor films.

With reduced bandtail disorder in NFAs, there is a low concentration of sub-bandgap states that can be occupied; thus, the thermal generation of carriers is suppressed, resulting in low thermal noise current. The experimental data demonstrate that minimizing bandtail disorder spread ΔE is key to reduce noise inherent in the materials. This approach complements prior strategies, such as injection blocking layers and links to efforts in controlling disorder through molecular design and structure–processing relationships. As such, the absorption spectra bandtail and the sub-bandgap DOS can serve as critical screening criteria to select materials with low disorder for future devices.

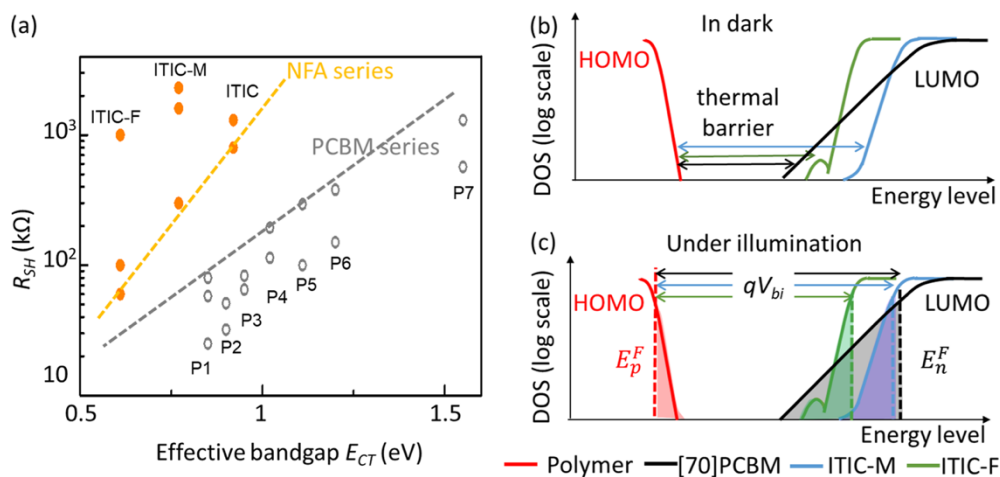
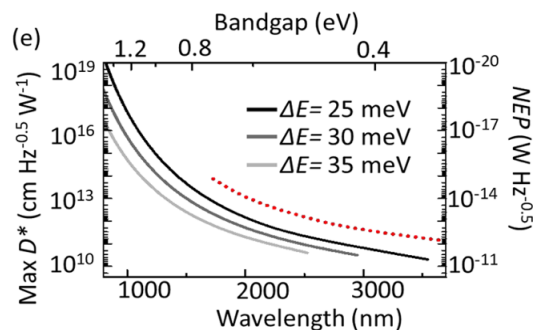


Figure 4. Shunt resistance of organic BHJ photodiodes as a function of the effective bandgap. The orange series are devices with the same polymer donor matched with different non-fullerene acceptors. The gray series are devices using different polymer donors with the acceptor [70]PCBM. The dashed lines are linear fits to the boundary of each series. Schematics of the electronic structures and carrier distributions for devices b in the dark and c under illumination. The shaded areas represent states filled up to the quasi-Fermi levels $E_{p/n}^F$ by photogenerated charges.

To further conceptualize our understanding of thermal noise in a general framework, we examined the dependence of thermal noise on the effective bandgap and bandtail disorder through a physical model, in which the DOS is modified to include sub-bandgap states. The calculations predict the photodiode noise level at zero bias for a range of E_{CT} and ΔE , and the predictions match very well with the measured values for three BHJs with different acceptors. This model quantifies the dramatic change in thermal carrier concentration due to the ΔE spread. Taking disorder into account, the model enables prediction of the maximum achievable detectivity (D^*) and the longest detectable wavelength in organic infrared photodiodes (see inset). The theoretical limits offer targets for future work on improving D^* and extending the range of detection wavelength of thin-film infrared photodiodes.



Photoconductive Detectors

To overcome the inherent challenges associated with exciton dissociation and blend systems, we collaborated with Jarret Vella from AFRL/RV to demonstrate the first example of a high-performance infrared photoconductor utilizing a donor–acceptor CP with broadband operation from the shortwave to longwave infrared. After a substantial materials synthesis and device screening effort, we found materials with novel attributes that enabled thin-film monolithic photoconductive detectors that when processed from solution demonstrate specific detectivities ranging from 2.10×10^9 to 8.01×10^{10} Jones (1 Jones = $1 \text{ cm Hz}^{1/2} \text{ W}^{-1}$), depending on the spectral region. These room-temperature detectivities are comparable to lead salts and closely approach those of cooled, state-of-the-art epitaxial devices based on InGaAs, InSb, and HgCdTe. This work provides a fundamentally new platform for broadly applicable, low cost, ambient temperature infrared optoelectronics. Figure 5 below shows the performance of our work (photodiodes labelled as “CP” and photoconductive detectors in red) demonstrating not only new and high performance for organics, but some of the highest detectivities overall spanning the SWIR-LWIR. It is straightforward to anticipate major improvements in performance considering these very preliminary results. Moreover, additional efforts and the development of a program with AFRL slated to begin FY 2021 alongside commercialization efforts.

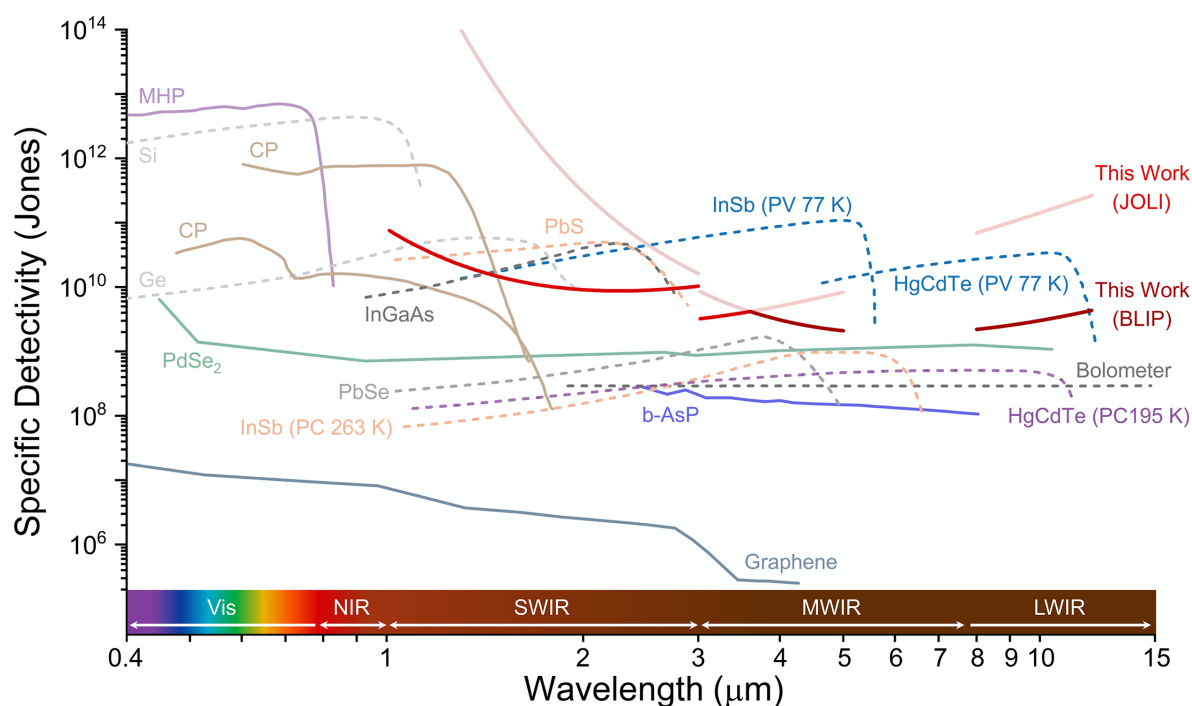


Fig. 5. Spectral D^* under JOLI and BLIP conditions for this photoconductive (PC) detector, compared with that of other detector technologies.

III. Conjugated Polymers with Open-Shell Electronic Structures

Work performed during this award established the first clear design paradigms for systematic control of the bandgap, which has revealed a thermodynamic tendency toward open-shell electronic structures in extended electronic systems (i.e. those with a greater degree of electronic coherence than “traditional” DA CPs). We have witnessed that narrow bandgaps afforded through extended conjugation are intimately related to the coexistence of nearly degenerate states, which can be tuned through synthetic design. The unique electronic structures and spin correlated phenomena arising from unpaired electron densities and the presence of magnetic moments coupled to light elements, offers richer categories of behavior than in closed-shell CPs. For example, these materials exhibit distinct optical, electronic, spin, and excited state properties whose structure and dynamics can be optimized for a wide range of applications. We have already demonstrated the utility of these materials in variety of high-performing technologies including: (1) intrinsically conductive and thermoelectric polymers in collaboration with AFOSR funded investigator Prof. Boudouris (Grant FA9550-15-1-0449, *Macromolecules*, **2018**, 51(10), 3886–3894); (2) IR photoconductive polymers (in collaboration with Dr. Vella, AFRL/RV, USM Disclosure No. 2020.0026, **2020**); (3) wide potential window supercapacitors with stable n-doped states (in collaboration with Prof. Ng, UCSD Electrical Engineering, *Adv. Energy Mater.* **2019**, 1902806); and (4) new excited state dynamics, tunable photophysics, quantum, and coherent phenomena (in collaboration with Prof. Sfeir, City University of New York (CUNY) Photonics Initiative). The new excited state dynamics measured in these systems are under investigation by AFRL scientists for a wide range of applications.

High-Spin Ground States

High-spin configurations offer new notions of spin manipulation, organic magnetism, quantum functionalities and interrelated (opto)electronic properties at the forefront of research efforts in diverse fields such as chemistry, materials science, and condensed matter physics. The intrinsic instability of this electronic configuration in light-element (carbon-based) materials complicates synthesis and precludes an understanding of how some of the most fundamental properties associated with the nature of the chemical bond (electron pairing) in organic materials manifest in practical applications. To this end, we implemented an entirely new macromolecular design paradigm, such that low bandgap CPs were synthesized in order to yield materials that are ground state triplets (high-spin) in their neutral form (Fig. 6). EPR, pulsed EPR, and superconducting interference device (SQUID) magnetometry are consistent with high-spin ($S = 1$) polymer chains; providing the first neutral, stable examples in the field.

Our approach is unique in that strong electron correlations give rise to: i) the narrowest bandgaps achieved in solution-processable CPs; ii) the first demonstration of intramolecular and intermolecular ferromagnetic coupling in mid-scale molecular systems; and iii) the first example of ground state triplets stabilized through extensive delocalization. These materials can be easily handled and show interrelated optoelectronic functionalities; contrasting significantly with the only other Kekulé ground state triplet, generated photochemically and examined spectroscopically in a cryogenic matrix. This picture also differs from electron rich nanographenes or graphene nanoribbons (GNRs), which localize unpaired electrons at the zigzag edges (Fig. 7), and face considerable difficulties in synthesis and stability. These studies overcome significant and historically rooted challenges associated with high-spin organic materials and open access to a broad variety of technologically relevant applications thought of as beyond the current scope of functional organic materials systems. For a detailed analysis of this material via EPR, pulsed EPR, SQUID, and quantum chemical calculations see our publication (*Sci. Adv.* 5, eaav2336 (2019) doi: 10.1126/sciadv.aav2336).

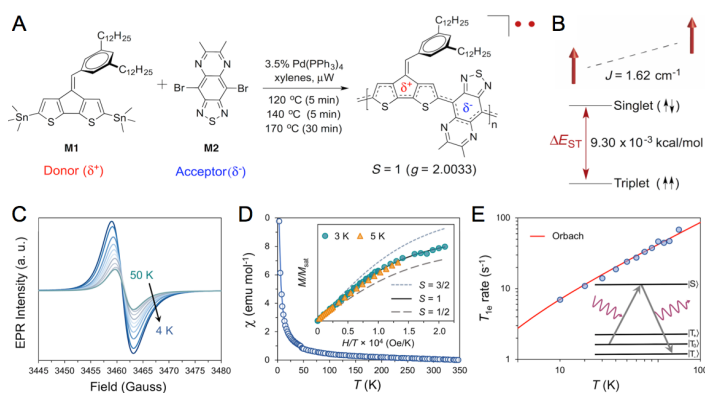


Figure 6. Synthesis and electronic structure of the first high-spin DA CP. (A) Polymerization and (B) magnetic properties exhibiting intramolecular ferromagnetic exchange coupling and a high-to-low spin energy gap $\Delta E_{ST} = 9.30 \times 10^{-3}$ kcal mol $^{-1}$. (C) EPR from 4 to 50 K indicating a paramagnetic ground state. (D) SQUID magnetometry of a solid sample. Main plot: Magnetic susceptibility (χ). Inset: Magnetic field (H) dependence of the magnetization (M) at 3 and 5 K, with Brillouin function for $S = 1$ diradical (E) Log-log plot of the X-band $1/T_{1e}$ recovery rates versus temp. fit by the temp. dependence of the Orbach-Aminov relaxation mechanism.

Connections Between Classes of Materials

Significant efforts were made over the course of our studies to characterize electronic structure in these extended π -conjugated systems. This challenge has gone largely unaddressed in the field. The connections between these classes of materials is far from established but can be framed within the context of conventional theories related to organic semiconductors (OSCs) and open-shell diradicals. Open-shell (diradical) character (y) is an important metric that provides insight into the ground state (GS) electronic configuration of molecular systems (see Fig. 7). Conceptually, y represents the degree of electron correlation or the effective bond-order. Because y also correlates to specific excited states, physicochemical properties concerned with those states are strongly correlated and distinct optical, transient, electronic, spin, and magnetic activities emerge. Various “biradicaloids” (defined as $0 < y < 1$) based on π -conjugated molecules have been developed including: oligoacenes, quinoidal oligothiophenes, polycyclic aromatic hydrocarbons (PAHs), nanographenes and polyradicaloids such as graphene nanoribbons (GNRs) (Fig. 7). General design guidelines involve embedding pro-aromatic quinoidal core structures into a π -framework, which upon aromatization (at the expense of

diminishing the covalency of a π -bond) results in resonance stabilization of the diradical form (Fig. 7) and a degenerate or (pseudo)degenerate partially occupied orbital manifold. Here, Clar’s rule for aromatic sextets, where the electronic configuration involving the greatest number of aromatic sextets (6 π -electrons) has the greatest contribution to the electronic properties of the system, is invoked to explain the high diradical character. The diradical character can also be controlled by the amount of resonance energy gained, substituent and structural effects, spatial distribution of the frontier MOs, and generally increases as the bandgap is reduced as a result of increased configuration mixing (HOMO-LUMO admixing) (Figs. 1 and 7). The energetics associated with aromatic stabilization and requirements on stability require larger systems, which remain theoretically intractable, difficult to synthesize and isolate, and whose properties are difficult to control, *despite significant efforts over the last 50 years*.

OSCs with embedded quinoidal subunits, extensive delocalization, and very narrow bandgaps have demonstrated open-shell electronic configurations in their neutral form, a property which has also recently been demonstrated in narrow bandgap donor-acceptor (DA) molecules and copolymers, with the vast majority of examples of polymer systems emanating from our research group. Our initial studies can be summarized in a very general manner with an energy level diagram (Fig. 8) in which the energies of the lowest singlet (S_0) and lowest optically-accessible singlet (S_1) relative to the lowest triplet (T_1) states fundamentally determine the properties of the molecules. In ‘conventional’ organic materials, exchange interactions are of moderate strength and the lowest triplet (T_1) and lowest optically-accessible singlet (S_1) energy gap is typically less than 1/3 the energy of the S_0 - S_1 gap. Our efforts focus instead on new emergent applications enabled by molecules that are described by intermediate and strong correlations, very narrow bandgaps, and open-shell character. In the limit of strong electron correlation ($y = 1$), T_1 becomes approximately equal or even lower than S_0 with the spin

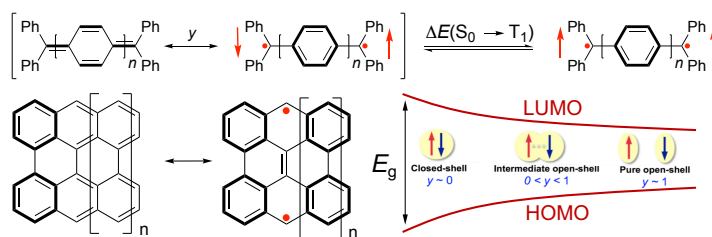


Figure 7. Diradical resonance contributors and evolution of diradical character as a function of narrowing the bandgap.

configuration being controlled by adjusting molecular parameters and the relative ordering of these states. In contrast to conventional approaches, extended electronic character, bandgap control at low energies, and the molecular size of polymers affords new design elements by which to access, stabilize, and tune these electronic configurations.

Such synthetic control has also resulted in novel optical, transport, transient, spin, thermal, and magnetic behavior not previously measured in soft-matter (polymer) systems. This discontinuity in the structure and dynamics of these materials as the bandgap continues to narrow is a manifestation of increasing electron correlations and, similar to inorganics, leads to new emergent properties. Moreover, these materials are multiscale in their characteristic energy, length, and time scales. For example, fundamental excitations span the Vis-IR (intra- and intermolecular excited state transitions), microwave (between different spin states), and beyond. The combination of these unique aspects: modularity, novel physics, and easy manipulation has enabled new optoelectronic and device functionalities that cannot be realized with current semiconductor technologies. These efforts and associated collaborative teaming are at the forefront of materials synthesis, spectroscopy, and devices.

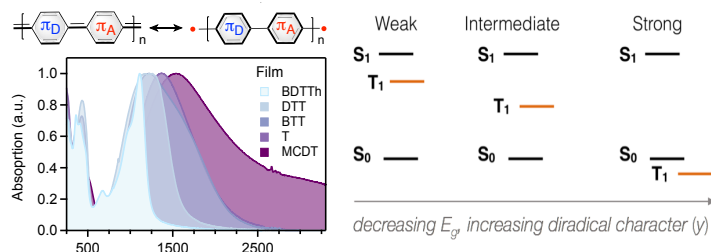


Figure 8. Absorption spectra (thin-film) of narrow bandgap DA copolymers with varying diradical character. (Right) The exchange interactions determine the energies of the triplet (T_1) state relative to the singlets (S_0 , S_1), which governs the optical, electrical, and magnetic properties of molecules.

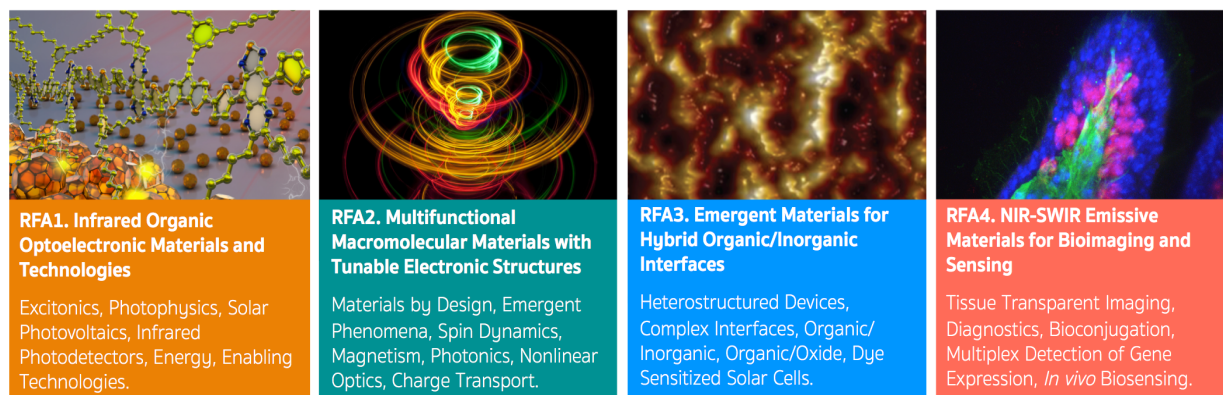
IV. Building Optoelectronics Infrastructure in the State of MS.

We have further translated the developments made in IR optoelectronics and control of electronic structure into a state-wide program and provided leadership in the state's infrastructure improvement grant from NSF entitled "Center for Emergent Molecular Optoelectronics (CEMOs)" awarded for \$20 million in late 2018. In 2018, Azoulay also built a state-of-the-art facility which has helped SPSE to attract new faculty, additional funding, house regionally distinct advanced materials characterization and device fabrication, engineering, and testing equipment. Clearly, none of this would have been possible without the initial investment by AFOSR and support of Dr. Caster and the AFOSR and AFRL teams. A brief description of these programs is below.

Center for Emergent Molecular Optoelectronics (CEMOs)

CEMOs is an interdisciplinary materials research program between the four MS research universities directed at critical and contemporary optoelectronic and energy challenges in key focus areas of fundamental science and engineering research not previously represented within the state. CEMOs is developing new, unified research methodologies to overcome fundamental limitations of organic semiconductors (OSCs) and addresses research grand challenges associated with: i) the integrated development and application of precision synthetic methods and sophisticated theoretical tools that afford insight into complex structure-property-performance relationships, ii) enabling the functionality of OSCs in the infrared (IR), and iii) controlling electronic structure to enable new functions, properties, multifunctional activities, and to

discover new phenomena. The four Research Focus Areas (RFAs) areas spanning many classes of soft-matter and hybrid technologies are in the Figure below.



Center for Optoelectronic Materials and Devices (COMD)

COMD, a center (9/2018) housed within SPSE features advanced instrumentation to conduct pure and applied research in emerging areas of soft matter and hybrid optoelectronics. The center currently benefits from state-of-the-art facilities for soft-matter optoelectronics research including newly acquired thin-film device fabrication and characterization equipment, SAX/WAXS laboratory beamline, XPS spectrometer with integrated UPS and Ar GCIS capabilities, magnetic characterization, AC/DC superconducting interference device (SQUID) magnetometer, electron paramagnetic resonance (EPR), cryogenic probe station, and supercomputing capabilities. COMD will serve as a hub to facilitate collaborative research across MS with a focus on advancing the integration of optical, electronic, spin, magnetic, quantum and interrelated properties in these materials for next generation devices and systems.

Conclusion

By continuing to build upon the fundamental properties of these narrow bandgap polymers, we have demonstrated novel capabilities, such as the detection of IR light, ground state electronics that can be manipulated, conductivities that are higher than other neutral organic solids and unique electrical, optical, spin, magnetic, thermal, and quantum behavior. We have discovered that this discontinuity in the structure and dynamics of these materials is a manifestation of increasing electron correlations and, similar to inorganics, leads to new emergent properties allowing for novel functionality. Moreover, these materials are multiscale in their characteristic energy, length, and time scales. For example, fundamental excitations span the ultraviolet/visible/IR (intramolecular excited state transitions), infrared (intermolecular excited state transitions), microwave (between different spin states), and beyond. Thus, synthetic control of the properties of conjugated polymers at low energies, the major objective of this work, has resulted in a multitude of new fundamental properties and technological capabilities of relevance to diverse DoD and AFOSR/AFRL technologies. This has been accomplished in the short time since the project has begun. The combination of the unique aspects of these materials: modularity, novel physics, and easy manipulation should enable new optoelectronic and device functionalities that cannot be realized with current semiconductor technologies. We are quite excited by these results and are confident that we will continue to lead in materials development and that various communities will begin to implement these materials. We further anticipate that

follow on efforts and collaborations with AFRL will be highly productive for advancing a multitude of new technologies.