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***

Here we overview selected NU achievements in realizing new molecular and polymeric organic semiconductors for TFTs, with emphasis on key TFT figures-of-merit achieved in novel architectures. This work was motivated by the fact that organic semiconductors 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 π-carrier mobility) in semicon-ducting polymers while maintaining solubility and processability; *ii*) exploring new π-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.

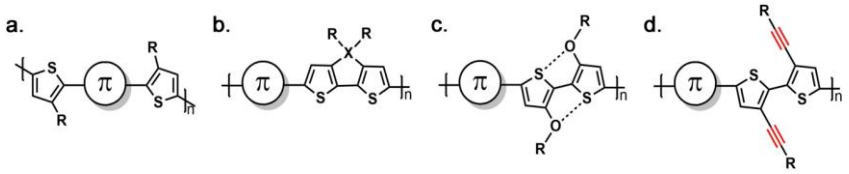



**Fig. 4**. Materials design strategies for polymer semiconductors with high degrees of backbone coplanarity: (**a**) inserting non-alkylated π-spacers; (**b**) conformational locking through covalent bonds; (**c**) conformational locking through intramolecular non-covalent interactions; (**d**) introducing "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 π-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 solidfied (**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 ternaaries. Strategy **4c** is a sterically-based strategy which places sp-hydbridized, non-bulky solubilizing alkynyl substituents at thiophene β-positions. The result is a family of π-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.

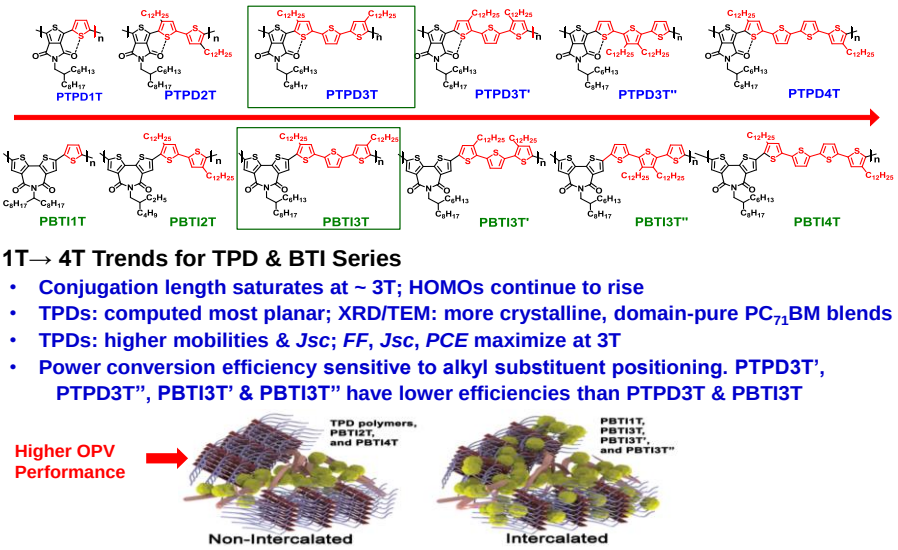



**Fig. 5.** Comparison of thiophene (T) extension effects on opto-electronic properties in donor-acceptor polymeric systems with conformational locking (**TPD**, top) and without conformational locking (**BTI**, bottom) to stabilize π-system coplanarity.

Focus *ii* explores a completely new connectivities for organic semiconductors, using diyne (-C≡C-C≡C-) linkages to impart combined torsional freedom while main-taining essentially uninterrupted π-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 π-conjugation as judged by optical and opto-electronic metrics. These inlcude good TFT mobilities and solar cell power conversion efficiencies.

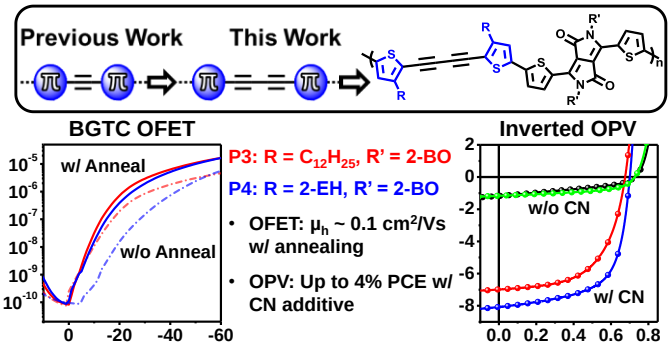



**Fig. 6.** Polymeric semiconductors employing torsionally flexible butadiyne linkages have good OFET mobilities and OPV power conversion efficiencies.

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

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 π-conjugated semi-conducting copolymers. Unlike the traditional Stille polycondensation, this DARP protocol eliminates the need for environmentally harmful, toxic organotin reagents. This DARP protocol employs low loadings of commercially available catalyst components and a green solvent. In this work, several representative π-electron copolymers were synthesized in excellent yields and high $M_n$, and were benchmarked vs Stille-derived counter-parts by close comparison of optical, NMR, FET, and electrochemical data; all indicate great chemical similarity and no significant structural defects in the DARP copolymers. The DARP and Stille copolymer and fullerene blend microstructural properties and morph-ologies were characterized with AFM, TEM, and XRD and are found to be virtually indistinguishable. Likewise, the charge generation, recombination, and transport characteristics of the fullerene blend films are found to be identical. For the first time, TFTs and OPVs fabricated with green DARP-derived copolymers deliver performance (8.4% efficiency) rivalling or surpassing Stille-derived materials. We believe that the entire organic electronics community will eventually adopt this methodology. Focus *iv* asks 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-electonic 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. Experimental and computational coarse grain modeling results reveal that systematic $M_n$ variation greatly influences both intrachain and interchain interactions, and ultimately the degree of phase separation and morphology evolution.

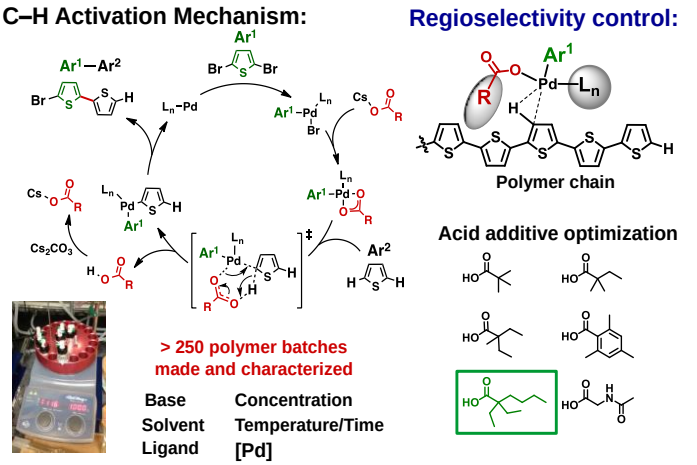



**Fig. 7**. Reaction pathway optimization to create green semi-conducting polymers via Direct C–H Arylation Polymerization (DARP).

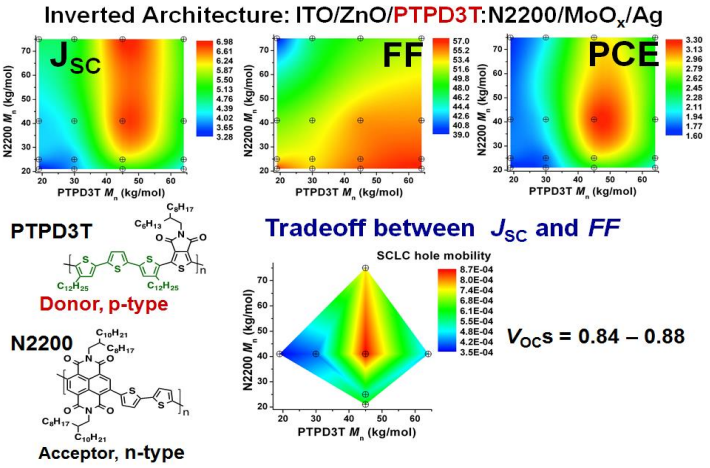



**Fig. 8**. Molecular masses and opto-electronic performance "sweet spot" for π-polymer- π-polymer blend films.

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 perylenediimide (PDI) small molecule acceptor (SMA) crystallinity and donor polymer aggregation and crystallinity effects on blend microstructures and the resulting opto-electronic 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.

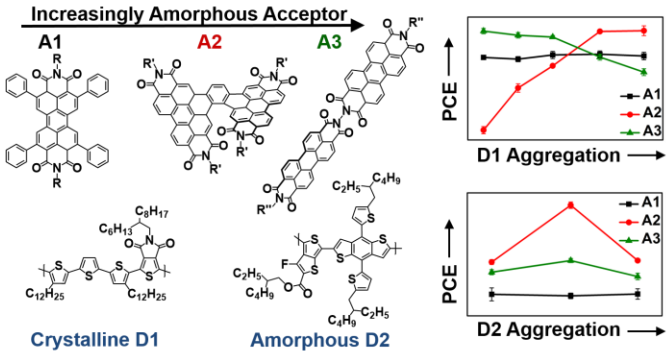



**Fig. 9**. The intriguing interplay of small molecule acceptor crystallinity and donor polymer aggregation on the power conversion efficiencies (PCEs) of photoactive blends.

***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, com-plex 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-π-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 π-system while at the same time preserving molecular polarizability. In the most recent work, we focused on intermolecular interactions between the π-building blocks in dielectric films. Note that film capacitance scales as the equation, $C_i = \frac{k\varepsilon_o}{d}$

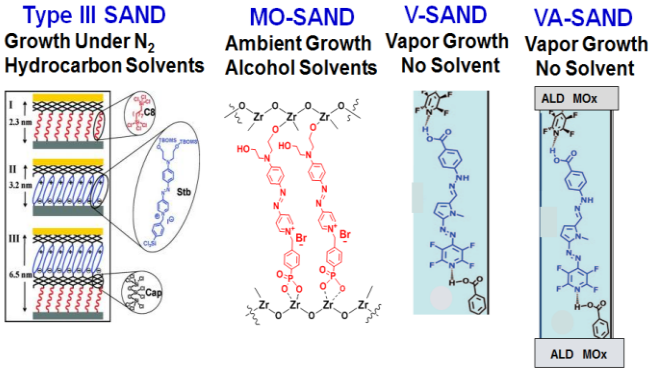



**Fig. 10**. Classes of self-assembled nanodielectrics (SANDs) created for specific properties and functions.

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.

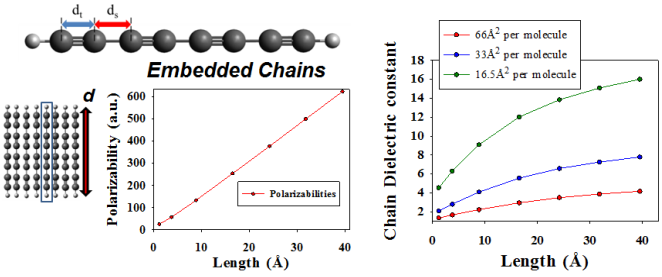



**Fig. 11.** Packing density effects on the dielectric constants of embedded polyynes of indicated lengths in SAND-type dielectric films.

***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 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 it's 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

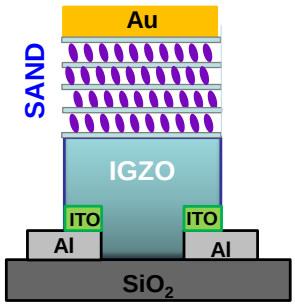



**Fig. 12**. Bottom contact, top gate combustion-processed a-IGZO TFT with a SAND gate dielectric. μ = 20 $cm^2$/Vs, $I_{on}/I_{off}$ = $10^6$.

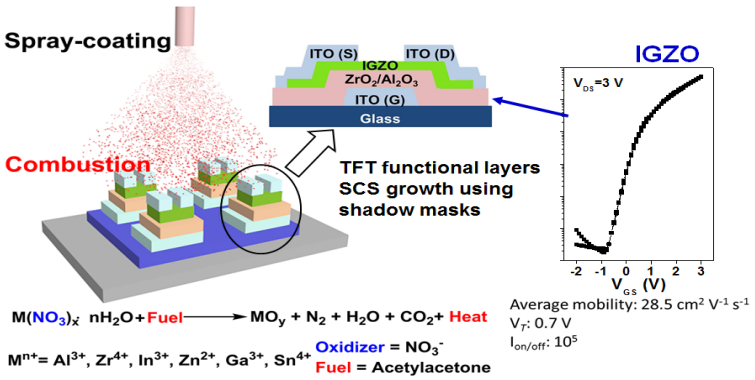



**Fig. 13**. All-oxide transparent high-performance a-IGZO transistors fabricated by spray combustion synthesis

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 (semi-conductor, 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 $In_2O_3$ + PVP, the resulting films are optically transparent, mechanically flexible, with μ ≈ 10 $cm^2$/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.

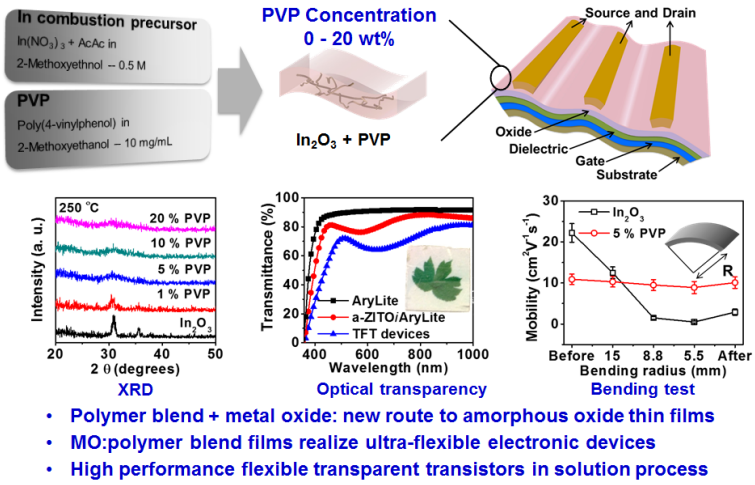



**Fig. 14**. Hybrid optically transparent, mechanically flexible, high-mobility polymer-amorphous oxide "alloys"

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

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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).