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Air-Stable n-type Conductors and Semiconductors

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14. ABSTRACT

This report summarizes results supported by grant no. FA9550-12-1-0190. We report: 1. Development of new n-type dopants 2. Design rules and synthesis of high performance n-doped conducting polymers; 3. Fundamental understanding of organic semiconductors through tuning molecular packing and morphology; 4. Stretchable semiconductor and dielectric material development.

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Technical summary

We have made major achievements during the funding period of this grant. We summarize the achievements based on area of research. Most the results summarized below have been published and details can be found in related publications. For the ones that are under review, we include a more detailed summary.

1. Development of n-type dopants:

We have developed several efficient n-type dopants and gained important fundamental understanding on their operating mechanism and design rules. We demonstrated a number of applications of the n-type dopants developed in this program to control the Dirac point of graphene, fabrication of all-carbon solar cells, fabrication of transparent and flexible graphene photodetectors and enabling high performance organic solar cells. Some of the dopants we reported are now available from Sigma-Aldrich Co. Several research groups have used our reported dopants for conducting electrodes, organic solar cells and thermoelectrics.

We have devoted significant time to understand the chemical mechanism of air-stable n-type dopants based on benzimidazolium salts and reduced benzimidazoles (**Figure 1**, DMBI-I and DMBI-H). We found that DMBI-H dopants react with fullerenes by a hydride transfer mechanism in solution. A consequence of this mode of reactivity is that the host material must form a C-H bond in the doping process; though, the reactivity is likely dependent on the specific materials combination. For combinations where hydride transfer is operative, such as fullerenes, the free energy for doping will be described by $\Delta G_{doping} = \Delta\Delta G_{C\text{-}H} + F(E^{0/-}_{A} - E^{+/0}_{D})$. The spontaneity of doping is dependent on the difference in the free energy of hydrogenation, $\Delta\Delta G_{C\text{-}H}$, of the dopant radical and neutral host. Thus, predicting the doping effect is a major challenge for DMBI-H dopants.

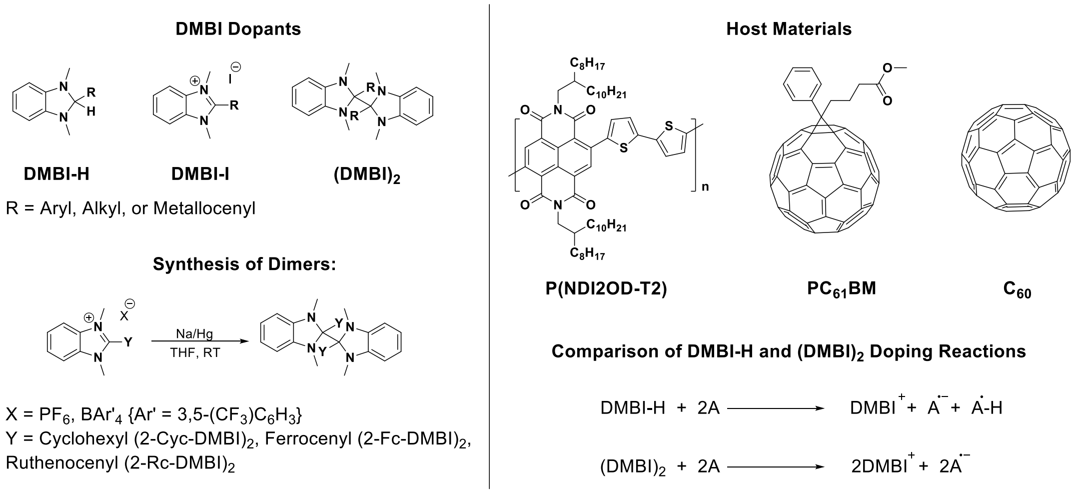

Figure 1: (Left) Various dimethylbenzimidazole (DMBI) based dopants, and the synthesis of DMBI dimers. (Right Top) Host electron transport materials used in this study. (Right Bottom) The basic doping reactions for an arbitrary organic semiconductor host, A, with either DMBI-H

or (DMBI)2 compounds. It is anticipated that both open-shell and closed-shell hydrogenated acceptor species, A•-Hn (n is odd) or A-Hn (n is even), form in the doping reaction depending on how many C-H bonds a given host forms.

We reported the neutral benzimidazoline-radical dimers (2-Cyc-DMBI)$_2$, (2-Rc-DMBI)$_2$ and (2-Fc-DMBI)$_2$ (**Figure 1**) and their use to form the doped state DMBI$^+$/A$^{\bullet-}$. The distinct properties of the (DMBI)$_2$ dopants relative to the DMBI-H dopants is evident from the solution doping rates, doped thin-film polaron band intensities, Fermi level shifts, and conductivities achieved using (2-Cyc-DMBI)$_2$ and its DMBI-H analog, 2-Cyc-DMBI-H, as dopants (**Figure 1 1**). Greater variability of the doping effect in the different hosts was found for the DMBI-H compound than for the (DMBI)$_2$ compound, which is attributed to the distinct reactions by which the two classes of dopants function. Notably, a very high room-temperature conductivity of 12.0 S cm^{-1} was obtained for C$_{60}$ doped with (2-Cyc-DMBI)$_2$. In contrast to the DMBI-H dopants, the free-energy for a dimer doping reaction is approximately described by $\Delta G_{doping} = \Delta G_{diss} - 2F(E^{0/-}_{A} - E^{+/0}_{D})$ where ΔG_{diss} is the free-energy for homolysis of the dimer carbon bond (first step, Mechanism I, Figure 1), $E^{+/0}$ is the reduction potential of the dopant cation, and $E^{0/-}$ is the reduction potential of the neutral polymer.

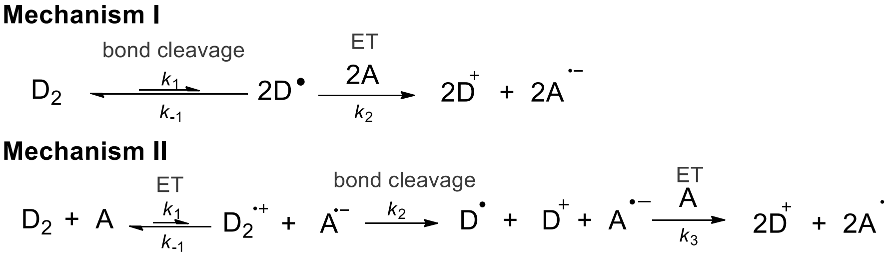

Figure 2. Mechanisms by which dimeric n-dopants (D$_2$) can react with acceptors (A).

We evaluated the thermodynamics of the (DMBI)$_2$ doping reaction by a combination of electron paramagnetic spectroscopy (EPR), and cyclic voltammetry (CV). Additionally, the doping mechanisms were evaluated by UV-Vis-NIR spectroscopy with a variety of host materials. EPR was used to measure the bond dissociation energies from the dimer into two monomer radicals. The thermodynamics of the dissociation reaction of (2-Fc-DMBI)$_2$ were determined to be $\Delta H_{diss} = +109$ kJ mol^{-1}, $\Delta S_{diss} = +163$ J mol^{-1} K^{-1}, and $\Delta G_{diss}(300\text{ K}) = +60$ kJ mol^{-1}. Using these parameters, the doping reaction free energy will be ~ 0 when $E^{0/-} = -1.93$ V. Notably, the most reducing isolable organic compound that is air-sensitive has a reduction potential of -1.95 V, whereas (2-Fc-DMBI)$_2$ is stable as a solid in air and of similar reducing strength. The mechanisms as determined by rate experiments in collaboration with the Marder group at Georgia Tech revealed that the dopants react by one of two mechanisms depending on the bond strengths of the dimers, the LUMO of the acceptor, and the temperature. In Mechanism I (**Figure 2**), dimer dissociation precedes electron transfer, and in mechanism II electron transfer is followed by dimer dissociation. In either case, the reaction results in two electrons reducing two equivalents of acceptor. Interestingly, the dimer with the weakest C-C bond, (2-Fc-DMBI)$_2$, reacted primarily by mechanism II with PCBM, but reacted by mechanism I with the weaker electron acceptor TIPS-pentacene. In contrast, (2-Cyc-DMBI)$_2$ which has an estimated ΔG_{diss} of 143.6 kJ mol^{-1} reacted by mechanism II with both acceptors.

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B. D. Naab, S. Himmelberger, Y. Diao, K. Vandewal, P. Wei, B. Lussem, A. Salleo, and Z. Bao, “High mobility N-type transistors based on solution-sheared doped 6,13-bis(triisopropylsilylethynyl)pentacene thin films,” Adv. Mater., vol. 25, no. 33, pp. 4663–4667, Sep. 2013.

H. Wang, P. Wei, Y. Li, J. Han, H. R. Lee, B. D. Naab, N. Liu, C. Wang, E. Adijanto, B. C.-K. Tee, S. Morishita, Q. Li, Y. Gao, Y. Cui, and Z. Bao, “Tuning the threshold voltage of carbon nanotube transistors by n-type molecular doping for robust and flexible complementary circuits.,” Proc. Natl. Acad. Sci. U. S. A., vol. 111, no. 13, pp. 4776–81, Apr. 2014.

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2. Design rules for high performance n-doped conducting polymers

We studied n-doping of several conjugated co-polymers based on perylene diimide (PDI) and napthalene diimide (NDI) acceptors co-polymerized with ethynylene, ethylene, and bithiophene by the dimeric dopant $(2\text{-Cyc-DMBI})_2$ (**Figure 3**). The n-doping reactions were confirmed in solution by UV-Vis-NIR spectroscopy and in thin films with photothermal deflection spectroscopy (PDS). The reduced species of the ethynylene-linked polymers were found to be more delocalized along the polymer backbone than the bithiophene-linked polymers by comparison of the absorption spectra (**Figure 4**). A high conductivity of 0.45 S cm^{-1} was measured for the ethynylene-linked polymer P(PDI2OD-A) which is among the highest reported conductivity for a solution n-doped polymer. In contrast, neither of the two bithiophene-linked polymers, P(NDI2OD-T2) and P(PDI2OD-T2), achieved conductivities greater than 4×10^{-3} S cm^{-1}. Furthermore, there is no correlation between the conductivity of the doped films and the mobility of the pure films, and GIXD measurements of the films find that a similar doped phase forms irrespective of the crystallinity of the pure host polymer. In absence of a significant difference in morphology, these results suggest a link between the polaron delocalization length of the polymers and the conductivity, and more fundamentally between the backbone structure of the polymer and the polaron delocalization length.

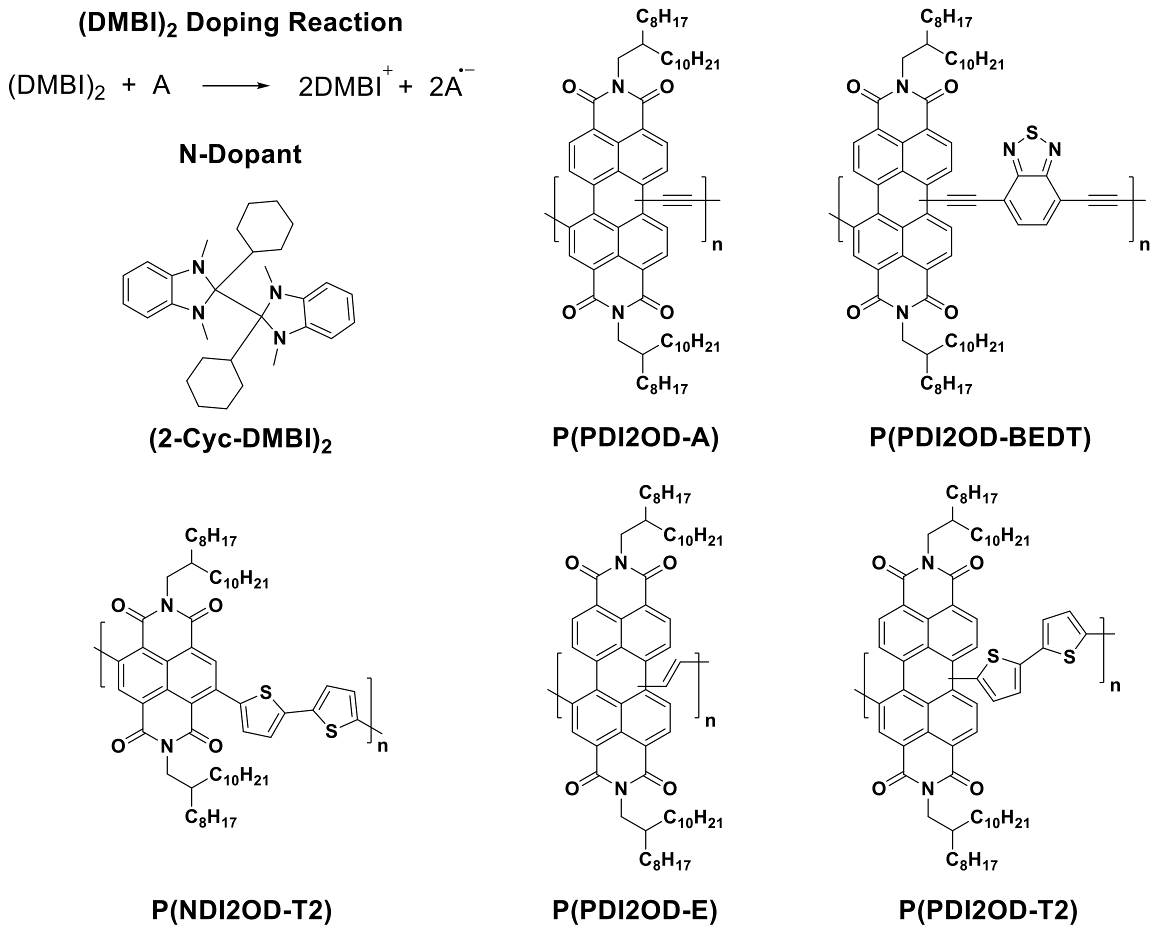

Figure 3: Structure of polymers used for the n-doping study by the dimeric n-dopant (2-Cyc-DMBI)$_2$.

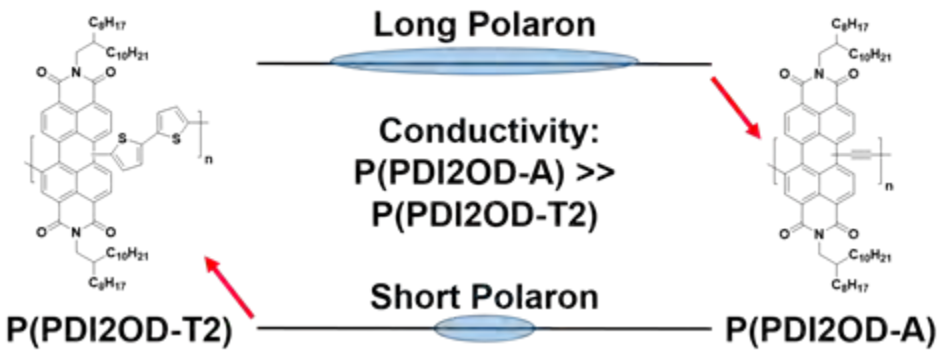

Figure 4: Summary of the major result from the structure-property study on the n-doping of PDI-based electron accepting polymers.

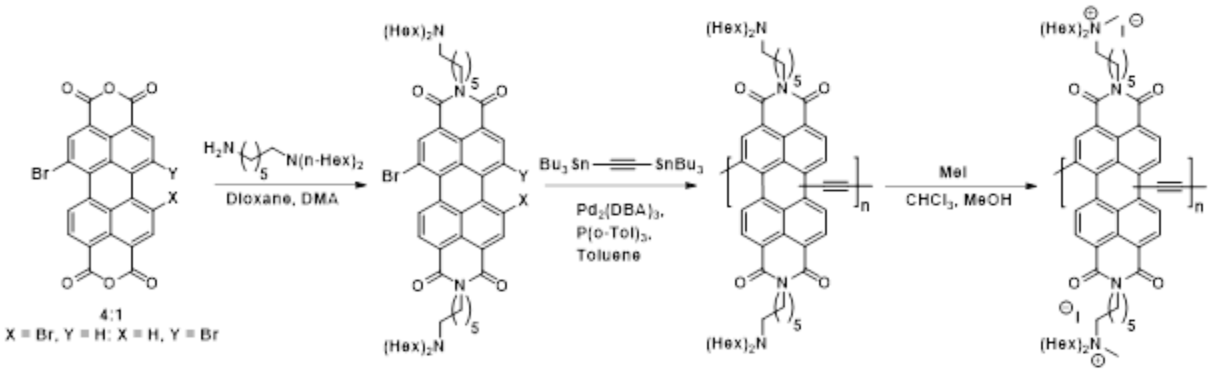

Figure 5: Derivatization of P(PDI2OD-A) to make self-n-doped tertiary amine and quaternary amine derivatives.

Modifications of the n-dopable polymer, P(PDI2OD-A), were then performed to attain a polar soluble self-n-doped polymer (**Figure 5**). Both amine and quaternary amine side-chain substitution lead to increased conductivity over undoped P(PDI2OD-A) (Figure 3). The effects of extrinsic n-doping by the dimer dopant (2-Cyc-DMBI)2 were evaluated spectroscopically in solution, by electrical measurements, atomic force microscopy, and grazing incidence x-ray diffraction. Interestingly, the quaternary amine substituted polymer is highly conductive and amorphous without extrinsic doping. The quaternary amine polymer is only soluble in polar solvents, and this property was exploited to fabricate an all polymer solar cell by orthogonal solvent processing to achieve a PCE of 4.2% (**Figure 6**). Both the amine and quaternary amine polymers exhibit sub-gap absorption features in air that are characteristic of a polaronic state. Extrinsic doping of the quaternary amine polymer rapidly initiates a phase change to a zwitterionic polymer with a crystalline structure. This result indicates that a highly crystalline conjugated polymer was prepared from an amorphous polymer simply by adding electrons to the backbone. The conductivity of the zwitterionic polymer was slightly higher with enhanced air-stability.

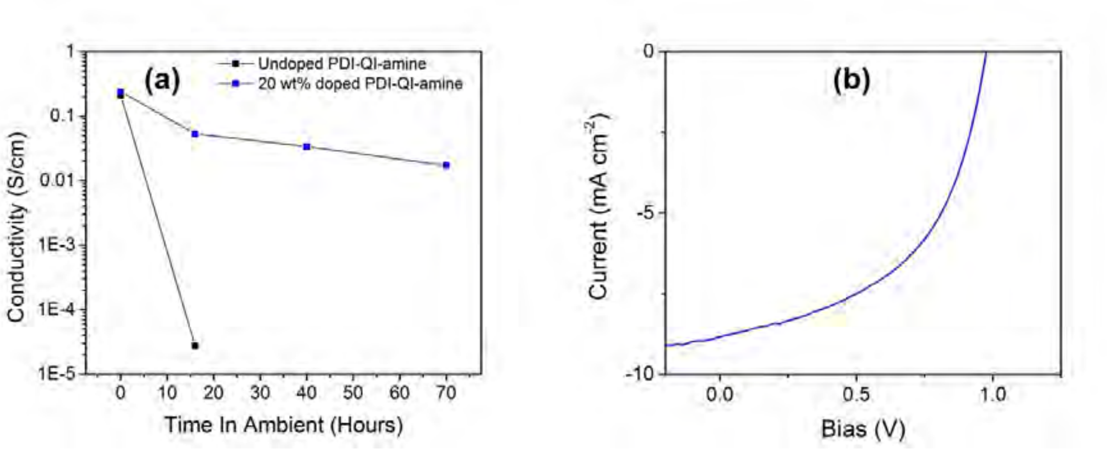

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Figure 6: (a) Comparison of the air-stability of the quaternary amine functionalized self-n-doped polymer, PDI-QI-amine, and 20 wt% $(2\text{-Cyc-DMBI})_2$ doped PDI-QI-amine, (b) J-V curve for all polymer solar cell with a PDI-QI-amine electron transport layer (PCE of 4.17%, J_{SC} of 8.75, V_{OC} of 0.96 V, and FF of 0.50).

Publications related to this topic:

B. D. Naab, X. Gu, Y. Zhou, T. Kurosawa, and Z. Bao, “High Conductivity Self-N-Doped Conjugated Polymers and Their Application as Electron Transport Layers in All Polymer Solar Cells,” J. Mater. Chem. A, vol. In Prepara, 2015.

B. D. Naab, X. Gu, T. Kurosawa, J. W. F. To, A. Salleo, and Z. Bao, “Role of Polymer Structure on the Conductivity of N-Doped Electron Accepting Polymers: Synthesis, Electrical, and Spectroscopic Characterization,” J. Am. Chem. Soc., vol. Submitted, 2015.

3. Fundamental understanding of tuning charge transport in organic semiconductors through molecular design, tuning molecular packing and morphology:

We have developed a number of novel methods to achieve unprecedented charge transport ability of organic semiconductors. Our methods were developed through fundamental understanding on tuning electronic structures through molecular design, molecular packing and morphology. The important aspect of our research is that our design rule keeps in mind the method for fabrication needs to be scalable. As a result, the materials we developed are highly processable and reproducible through solution coating and the fabrication methods we reported are scalable methods that can be potentially translated into large-scale production. Additionally, the high performance semconductors developed through our work enabled high performance polymer solar cells, transparent display back plane, and high stable organic transistor sensors for marine environment and disease diagnosis.

Organic semiconductors with higher carrier mobility and better transparency have been actively pursued for numerous applications, such as flat-panel display backplane and sensor arrays. The carrier mobility is an important figure of merit and is sensitively influenced by the crystallinity and the molecular arrangement in a crystal lattice. Here we describe the growth of a highly aligned meta-stable structure of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) from a blended solution of C8-BTBT and polystyrene by using a novel off-centre spin-coating method. Combined with a vertical phase separation of the blend, the highly aligned, meta-stable C8-BTBT films provide a significantly increased thin film transistor hole mobility up to 43 cm2 Vs−1 (25 cm2 Vs−1 on average), which is among the highest value reported to date for all organic molecules. The resulting transistors show high transparency of >90% over the visible spectrum, indicating their potential for transparent, high-performance organic electronics.

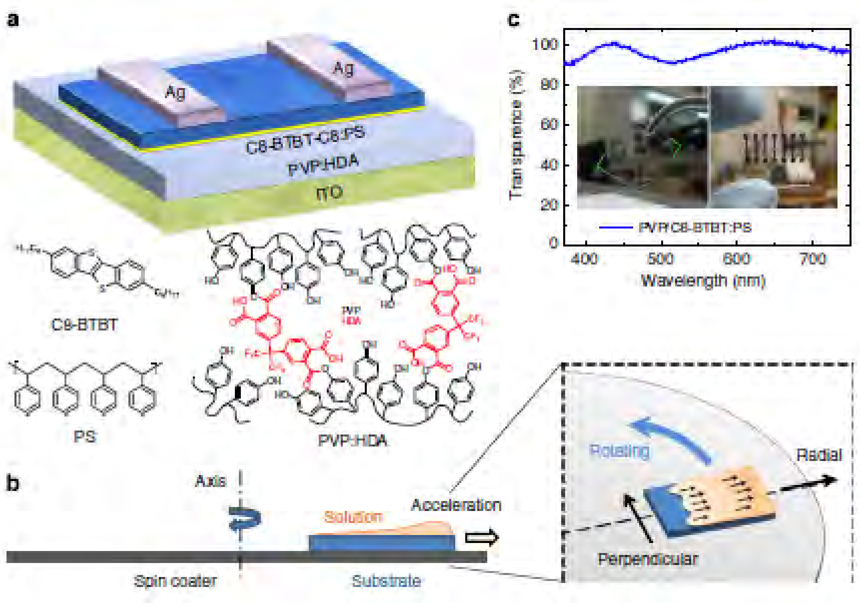

Figure 7. (a) Device configuration (b) Schematic representation of off center spin coating method (c) Transparency of off center spin coated C8-BTBT / PVP:HDA films.

Though the off center spin coating method enables very high performance organic transistors it is not very compatible with large areas. In contrast, the solution shearing method described by our group previously is compatible with large area substrates. 6,13(bis-triisopropylsilylethynyl)pentacene (TIPS-pentacene), a small-molecule organic semiconductor, adopts metastable polymorphs possessing significantly faster charge transport than the equilibrium crystal when deposited using the solution-shearing method. Here, we use a combination of high-speed polarized optical microscopy, in situ microbeam grazing incidence wide-angle X-ray-scattering and molecular simulations to understand the mechanism behind formation of metastable TIPS-pentacene polymorphs. We observe that thin-film crystallization occurs first at the air–solution interface, and nanoscale vertical spatial confinement of the solution results in formation of metastable polymorphs, a one-dimensional and large-area analogy to crystallization of polymorphs in nanoporous matrices. We demonstrate that metastable polymorphism can be tuned with unprecedented control and produced over large areas by either varying physical confinement conditions or by tuning energetic conditions during crystallization through use of solvent molecules of various sizes.

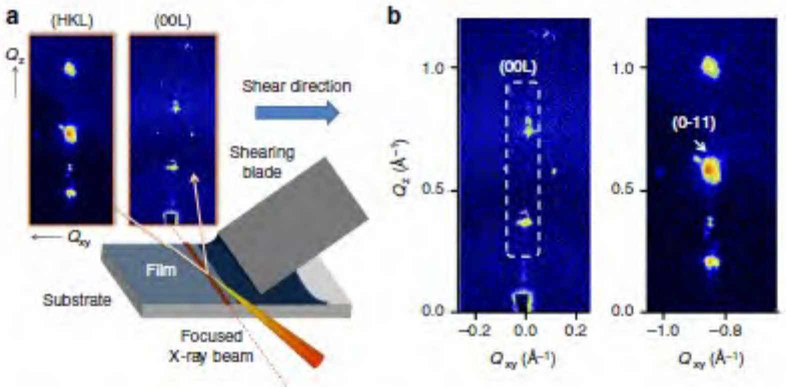

Figure 8. (a) Schematic of in situ x-ray diffraction of solution sheared TIPS-pentacene films (b) Scattering regions of solution sheared TIPS-pentacene captured by the high speed GIWAXS detector.

To demonstrate the applicability of solution shearing to large areas we then developed a method to deposit patterned transistor arrays of TIPS-pentacene. In our work, we use a simple chemical pre-patterning method to enable the solution shearing deposition of TIPS-pentacene on substrates with feature sizes as small as 100 µm. A schematic of our process is shown in Figure x. Grazing incidence x-ray diffraction (GIXD) was also used to confirm the existence of high performance TIPS-pentacene polymorphs in the patterned thin films. Mobilities as high as 1.13 cm2 V_1 s_1 were obtained on 400 µm wide patterns by depositing a high-performance, metastable polymorph of TIPS-pentacene.

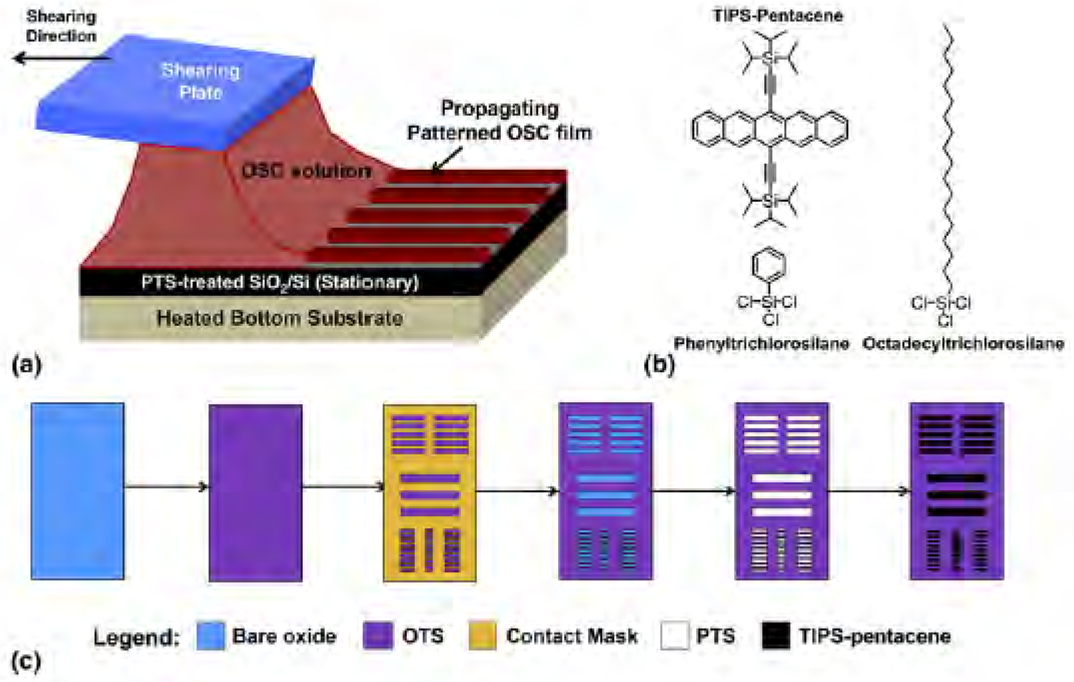

Figure 9. (a) Schematic solution shearing setup for the deposition of patterned organic semiconductors (b) Chemical structures of TIPS-pentacene, phenyltrichlorosilane, and octadecyltrichlorosilane (c) Illustration of the patterning method.

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L. Fang, Y. Zhou, Y. X. Yao, Y. Diao, W. Y. Lee, A. L. Appleton, R. Allen, J. Reinspach, S. C. B. Mannsfeld, and Z. Bao, “Side-chain engineering of isoindigo-containing conjugated polymers using polystyrene for high-performance bulk heterojunction solar cells,” Chem. Mater., vol. 25, no. 24, pp. 4874–4880, 2013.

J. Mei and Z. Bao, “Side chain engineering in solution-processable conjugated polymers,” Chem. Mater., vol. 26, no. 1, pp. 604–615, 2014.

4. Stretchable and self-healing materials and device development.

Future electronic devices will have unprecedented functions, robustness and capabilities if we can incorporate mechanical characteristics of skin. Therefore, skin-inspired electronics opens up a new field in electronic materials and device development. Our group is in the forefront of this emerging research field. We have reported several new electronic materials and devices concepts under this grant support. Specifically, we developed a new type of composite material that can self-heal at room temperature repeatedly and have electrical conductivity. Such materials, mimicking human skin functions, may have applications in electronic devices and coatings. We have developed understanding on materials design for high mechanical strength and stretchability. Finally, we have fabricated organic transistors with high stretchability.

Organic stretchable electronics have attracted extensive scientific and industrial interest because they can be stretched, twisted, or compressed, enabling the next-generation of organic electronics for human/machine interfaces. However, identifying suitable stretchable electronic materials and accurate measurements of their electrical properties when stretched remains a considerable challenge. Here we report a facile method to efficiently identify suitable semiconducting polymers for organic stretchable transistors using soft contact lamination. In our method, the various polymers investigated are first transferred on an elastomeric poly(dimethylsiloxane) (PDMS) slab and subsequently stretched (up to 100%) along with the PDMS. The polymer/PDMS matrix is then laminated on source/drain electrode-deposited Si substrates equipped with a PDMS dielectric layer. Using this device configuration, the polymer semiconductors can be repeatedly interrogated with laminate/delaminate cycles under different amounts of tensile strain. From our obtained electrical characteristics, e.g., mobility, drain current, and on/off ratio, the strain limitation of semiconductors can be derived. With a facile soft contact lamination testing approach, we can thus rapidly identify potential candidates of semiconducting polymers for stretchable electronics.

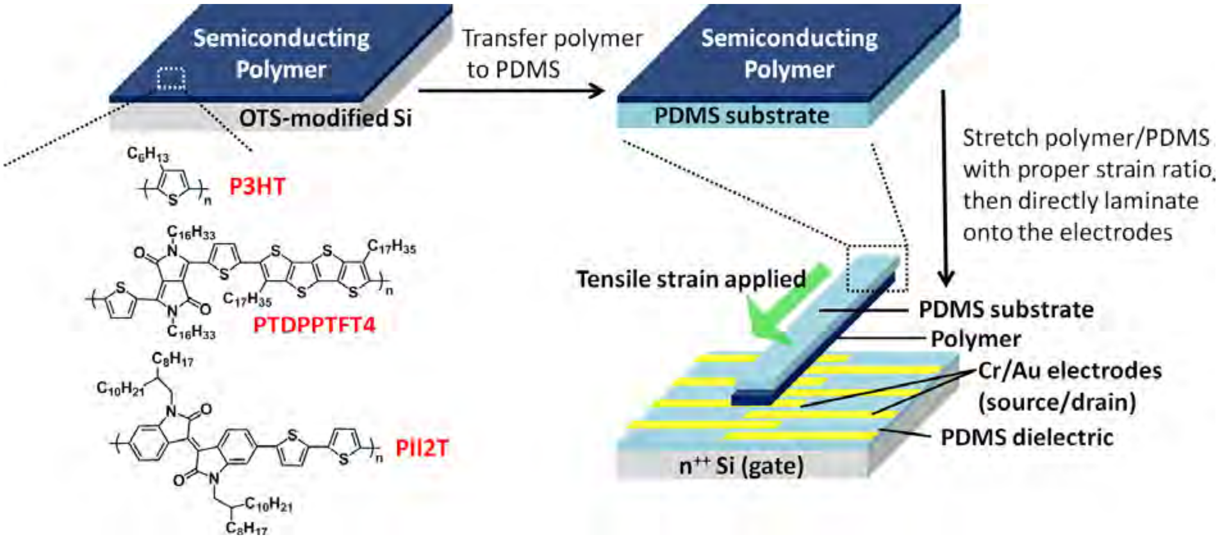

Figure 10: Schematic illustration of our lamination method used to evaluate semiconducting polymers for stretchable electronics. The chemical structures of the polymer evaluated in this work are shown as an inset.

Building upon our previous work with nickel nanostructured micro-particle polymer composites we then developed an elastic nanocomposite material with the ability to rapidly self-heal at room temperature by combining the unique features of hydrogen-bonded polymer and graphene oxide (GO) as a macro-crosslinker. Importantly, it also possesses mechanical strength comparable to commercial rubbers. Incorporation of GO enabled our composite with good mechanical strength; while the hydrogen bonding network within the polymer chains provide self-healing capability. GO is the oxidized form of graphene and has been established for its high-mechanical strength, large surface area and its ease for chemical modifications. The advantage of using GO instead of other typical crosslinkers is that only a small amount of GO is needed to achieve a dramatic improvement in the mechanical property of the composite, due to the multiple reactive sites on GO and its high mechanical strength. As a result, the density of available hydrogen bond sites (highly critical for self-healing) is not significantly reduced. In specific, we observed that by adding as little as < 2 wt% of GO to the polymer, we obtained an elastic material (elastomer) with similar mechanical property to that of conventional rubbers, while possessing a very fast healing speed at room temperature. Our obtained nanocomposite displayed a fast spontaneous self-healing and can heal up to 50% of its pristine extensibility in ~1 min in the absence of any healants, plasticizer, solvents, or external energy, while complete mechanical healing can be completed in ~1 hr.

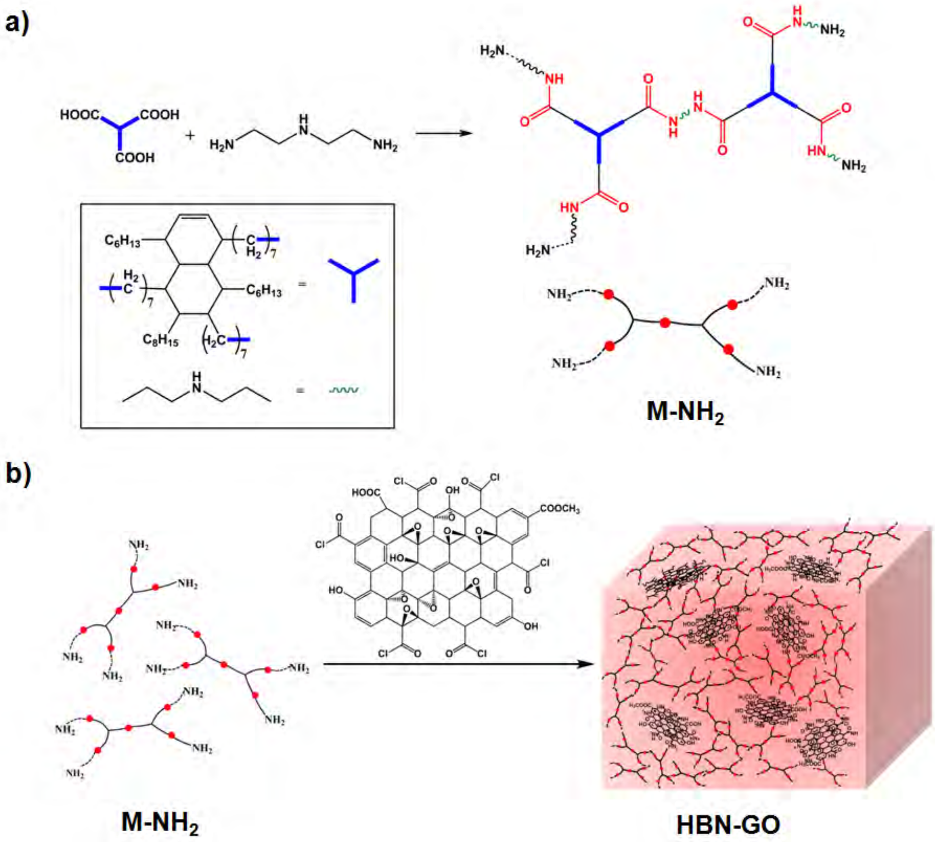

Figure 11. Stretchable self-healing material made with graphene oxide crosslinkers.

Publications related to this topic:

H. C. Wu, S. J. Benight, A. Chortos, W. Y. Lee, J. Mei, J. W. F. To, C. Lu, M. He, J. B. H. Tok, W. C. Chen, and Z. Bao, "A rapid and facile soft contact lamination method: Evaluation of polymer semiconductors for stretchable transistors," Chem. Mater., vol. 26, no. 15, pp. 4544–4551, 2014.

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Full Publication List:

[1] B. D. Naab, X. Gu, Y. Zhou, T. Kurosawa, and Z. Bao, "High Conductivity Self-N-Doped Conjugated Polymers and Their Application as Electron Transport Layers in All Polymer Solar Cells," *J. Mater. Chem. A*, vol. In Prepara, 2015.

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Patent inventions filed under this grant:

Stanford Docket #	Title	Inventors	Patent filing status
S14-135 (LC)	Stretchable Transistor	Bao, Zhenan /Chortos, Alex L /Hwang, Sung Woo /Kim, Tae Ho	South Korea Original 10-2014-0036127 3/27/2014 (Pending)
S14-024 (LC)	Enhancement of Skin-adaptability and bio-signal Detection using Micro-hairy	Bao, Zhenan /Pang, Changhyun	USA Utility (not yet filed) USA Provisional 62/023,684 7/11/2014 (Pending)

	structures for health-monitoring pressure sensor		
S13-491 (LC)	Pressure-Sensitive Electrode Material, Means and Methods of Use	Bao, Zhenan /Chortos, Alex L /Pan, Lijia	USA Provisional 61/917,271 12/17/2013 (Expired) USA Utility 14/573,928 12/17/2014 (Pending) PCT Original PCT/US2014/070929 12/17/2014 (Pending)
S13-403 (LC)	New Polymer Dielectrics for Transistors	Bao, Zhenan /Lee, Wen Ya /Schweicher, Guillaume /Wang, Chao	USA Provisional 61/980,390 4/16/2014 (Expired) USA Utility 14/688,683 4/16/2015 (Pending) PCT Original PCT/US2015/026167 4/16/2015 (Pending)
S12-437 (LC)	Self-Healing Electrode for Lithium Ion Battery	Bao, Zhenan /Cui, Yi /Tee, Chee-Keong /Wang, Chao /Wu, Hui	China Original (not yet filed) USA Provisional 61/724,838 11/9/2012 (Expired) USA Utility 14/075,841 11/8/2013 (Pending) PCT Original PCT/US2013/069326 11/8/2013 (Expired)
S12-422 (LC)	Self-healing conductive composites	Bao, Zhenan /Tee, Chee-Keong /Wang, Chao	Not filed
S12-233 (LC)	Nonvolatile doped organic memory devices	Bao, Zhenan /Lee, Wen Ya	Not filed
S11-378 (LC)	All carbon based solar cell and semiconductors	Bao, Zhenan /Ramuz, Marc /Vosgueritchian, Michael	USA Provisional 61/542,672 10/3/2011 (Expired) USA Utility 13/573,726 10/3/2012 ; 8,866,265 10/21/2014 (ISSUED)
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FA9550-12-1-0190

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

Zhenan Bao

Program Manager
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Abstract

This report summarizes results supported by grant no. FA9550-12-1-0190. We report: 1. Development of new n-type dopants 2. Design rules and synthesis of high performance n-doped conducting polymers; 3. Fundamental understanding of organic semiconductors through tuning molecular packing and morphology; 4. Stretchable semiconductor and dielectric material development.

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