ACS Partner Journal

ACCOUNTS of materials research

pubs.acs.org/amrcda

Viewpoint

Organic Iono-Electronics, a New Front for Semiconducting Polymers to Shine

Aristide Gumyusenge*

Cite This: *Acc. Mater. Res.* 2022, 3, 669−671

Read Online

ACCESS | Metrics & More | Article Recommendations

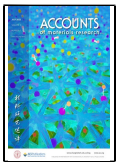
Structural tunability, low-cost solution processability, mechanical deformability, and biocompatibility were among several keywords that made organic semiconductors a popular class of materials.[1] Here we are over three decades later with very few practical devices using organic semiconductors, and many wondering what is next for the field of organic electronics and whether organics were destined for nothing more than low-grade electronics and displays.[2,3] The two main areas where organic materials were expected to thrive over their inorganic counterparts are the development of next-generation body−machine interfaces and advanced healthcare electronics.[4,5] One can argue that several research groups have been more than successful demonstrating the properties listed above, separately, and that the field has lacked concerted efforts to demonstrate real products. One can also argue that perhaps the financial burden for acquiring the needed taskforces for combining materials design and synthesis, device fabrication and characterization, and biointegration is a major reason why such demonstrations remain rare in laboratories. Instead, the industrial platforms (a good recent example being Neuralink) are now the sole players bringing together teams of chemists, engineers, and surgeons to prototype next generation neuroprosthetists that were long promised to be the epitome of organic electronics. The question then becomes whether despite the potential and recent advances, organic electronics are a dying field of research or whether only a few and pricy products will be realized. Regardless of the underlying logistical reasons, there remain fundamental challenges that ought to be addressed before we can witness the rise organic electronics.

To develop body-machine interfaces, the following are needed: (1) mechanical compliance,[4,7] (2) operational stability in physiological environments,[8] (3) reliable harnessing, discerning, amplification, and transduction of physiological information,[9,10] and (4) ability to adapt or learn from physiological surroundings and execute tasks accordingly.[11,12] Next generation healthcare devices, in addition to the features above, must monitor patients' vitals selectively and accurately, and bear a drug-delivery or healing function. These two thrusts have been proposed to employ iono-electronics, i.e. devices able respond to ionic signals and provide an output resulting from a material's property change upon ionic intercalation. To realize this ionically controlled multiresponsiveness, electrolyte gated transistors (EGTs)[11] are sought after as the fundamental building blocks for advanced electronics (Figure 1). In such devices, a semiconductor will typically respond to incoming ionic species and undergo a property change (electronic, optical, mechanical) which is in turn detected or utilized for a specific application. Though this is the author's viewpoint on the role of organic semiconductors in biointerfacing and healthcare applications, other research areas such as energy conversion and storage, displays, neuromorphic computing, and actuators[6] are also envisioned to benefit from advances in developing novel high-performance organic materials, especially mixed ionic-electronic conductors.

When targeting all the requirements listed above, it seems both surprising and concerning that only a few materials have been studied thus far.[11] The current approach for selecting iono-electronic materials, especially semiconductors, has been to directly borrow systems that have been shown to perform well in more mature device architectures (such as organic field-effect transistors) and repurpose them for various functions. This approach typically targets good electronic conductors, which has made poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) the most widely studied material for the applications mentioned above.[13,14] This is despite its (i) complex composite-based processing, (ii) low thermal tolerance for integration in circuits manufacturing, and (iii) poor control of its electronic and ionic components, not to mention its (iv) unalterable structure. Other successful examples in literature seem to address one challenge at a time[6] and lack a systematic, concerted, and application-driven materials design. A better approach seems to design polymers from the bottom up and realize the targeted property change depending on the application. Conjugated (semiconducting) polymers are ideal here owing to their structural versatility and multiresponsiveness.

Semiconducting polymers, simplistically speaking, are composed of a conjugated backbone flanked with solubilizing side chains. One can think of (in theory) unlimited combinations of building blocks and blend combinations based on conjugated units. Side chain and backbone engineering remain effective tools to design new semiconducting polymers. The key aspect for iono-electronics, especially EGTs, becomes systematic

Received: January 31, 2022
Published: July 4, 2022



https://doi.org/10.1021/accountsmr.2c00022
Acc. Mater. Res. 2022, 3, 669−671

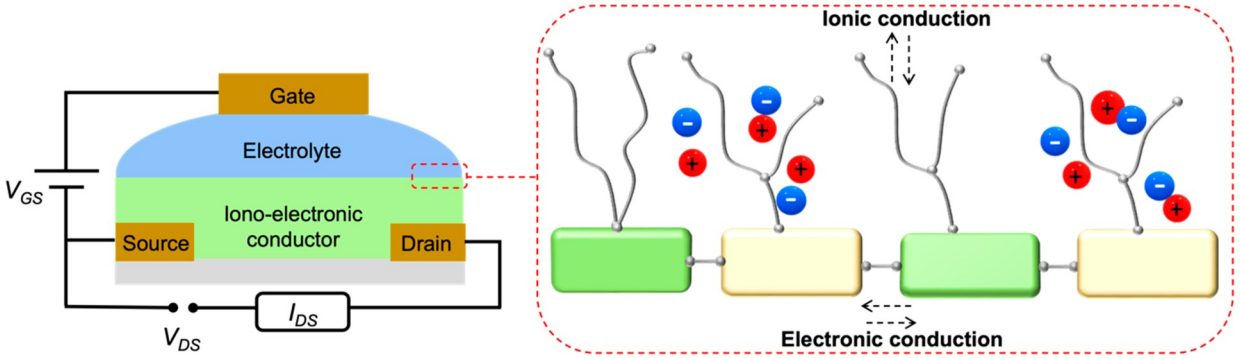


Figure 1. Organic iono-electronics as a new front for semiconducting polymers to shine. Electrolyte-gated transistors are envisioned as a platform to benchmark novel mixed ionic-electronic conducting materials. To impart balanced conduction, side chains and backbone engineering are effective tools for research groups to engineer new polymers toward advanced organic electronics, especially for smart biointerfaces and healthcare devices.

control of the ionic and electronic conduction of the polymeric semiconductor.[6] Side chains can be successfully used to solvate the incoming ions (by utilizing polar side chains) and the conjugated backbone can be used to tune the transport of ionically induced electronic charges, as shown in Figure 1. Copolymeric semiconductors would be ideal for such balance. Traditional polymers (e.g., diketopyrrolopyrrole, isoindigo, or naphthalenediimide-based polymers[15]), though ideal for facile synthesis and structural tuning, bear long alkyl chains and are thus hydrophobic and not optimal for iono-electronic devices. However, several research groups possess in-lab knowhow on a variety of conjugated backbones (for instance donor−acceptor building blocks studied for transistor devices, electrochromic displays, and solar cells)[15] that, once molecularly redesigned, can meet the above-discussed performance requirements in iono-electronics and potentially rival the most commonly studied candidate (PEDOT:PSS). This reopens the research on organic semiconductors and the design of new materials able to (i) interface with biology, (ii) operate in a variety of environments, (iii) offer tunable molecular and microstructural properties, and (iv) enable further composite designs.

To interface with biology, polar side chains imparting operation in aqueous media are ideal and more research is needed on (i) optimizing the placement and the density of these polar groups without hindering the electronic transport along the conjugated backbone, (ii) controlling ionic uptake by the semiconducting films, its impact on operational voltages, and the durability of resulting devices, and (iii) their impact on microstructural engineering in polymer films. Microstructural engineering becomes a vital tool in these materials, especially toward the realization of extrinsic properties such as mechanical deformation,[16] chain crystallization,[17] and addressing poor thermal and environmental tolerance shortcomings found in most organic semiconductors.[18] When designing novel microstructures, however, researchers must be sure to retain the capacitive and electronic features discussed above. To achieve adaptive functions at the body interface, controllable charge modulation and retention upon ionic uptake needs to be achieved and operational robustness is needed to mimic the high frequency signal transmission.[19,20] In combination with drug-delivery strategies, wound healing designs, and loop feedback controls, adaptive healthcare devices are envisioned.[21] It seems self-evident that multifunctional polymers should be further explored as opposed to repurposing a few candidates.

It is beyond debate that organic semiconductors have been kept out of the traditional CMOS electronics due to lower charge carrier mobilities as well as inferior thermal robustness for foundry compatibility (compared to inorganic counterparts). However, the structural tunability of conjugated polymers earns them a role that inorganics are not suited to play. Iono-electronics is a front where organic semiconductors hold an edge to deliver multifunctional devices. In these electronics, extremely high electronic conduction is not a requirement. Instead, a well-balanced mixed ionic-electronic conduction is needed. These electronics will undoubtedly benefit from the versatility of organic semiconductors, but fundamental research on their capabilities ought to be carried out and their role must be redefined.

To enable the next leap for organic iono-electronics, research groups should probe ionic insertion into semiconducting films, the resulting property change, and its impact on electronic charge modulation along the semiconducting chains. By relating structure to property and device performance, molecular fine-tuning strategies once again become available for meeting specific needs, and for addressing stability issues toward scalable manufacturing of functional circuitries. This route seems more reliable than the current approach that only targets a few polymer candidates and relies solely on engineering approaches to repurpose them. My research group will take this bottom-up approach and design/synthesize multifunctional polymers and polymer composites for future organic electronics. This viewpoint communicates our research motivation and what we believe is a novel front for organics to deliver on their longstanding promise for ubiquitous smart electronics.

AUTHOR INFORMATION

Corresponding Author

Aristide Gumyusenge − *Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0003-4995-5222; Email: aristide@mit.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/accountsmr.2c00022

Notes

The author declares no competing financial interest.

https://doi.org/10.1021/accountsmr.2c00022
Acc. Mater. Res. 2022, 3, 669−671

Biography

Aristide Gumyusenge received a BS in chemistry as a Rwanda Presidential Scholar at Wofford College in 2015, and a Ph.D. in chemistry from Purdue University in 2019 advised by Prof. Jianguo Mei. He was then the 2020 GLAM postdoctoral fellow at Stanford University where he worked with Prof. Zhenan Bao and Prof. Alberto Salleo. His research background and interests are in semiconducting polymers, their processing and characterization, and their unique role in the future of electronics. Particularly, he has tackled long-standing challenges in operation stability of semiconducting polymers under extreme heat and has pioneered high-temperature plastic electronics. He has been selected as a PMSE Future Faculty Scholar (2021), the GLAM Postdoctoral Fellow (2020–2022), and the MRS Arthur Nowick and Graduate Student Gold Awardee (2019), among other recognitions. Currently, he is an Assistant Professor of Materials Science and Engineering at MIT, where he leads the Laboratory of Organic Materials for Smart Electronics (OMSE Lab) starting January 2022. He holds the Merton C. Flemings (1951) Career Development Professorship.

REFERENCES

(1) Shaw, J. M.; Seidler, P. F. Organic Electronics: Introduction. *IBM J. Res. Dev.* **2001**, *45* (1), 3–9.

(2) Crawford, G. P. Flexible Flat Panel Display Technology. *Flexible Flat Panel Displays* **2005**, *25* (April), 1–9.

(3) Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. Paper-like Electronic Displays: Large-Area Rubber-Stamped Plastic Sheets of Electronics and Microencapsulated Electrophoretic Inks. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98* (9), 4835–4840.

(4) Someya, T.; Bao, Z.; Malliaras, G. G. The Rise of Plastic Bioelectronics. *Nature* **2016**, *540* (7633), 379–385.

(5) Lee, Y.; Lee, T.-W. Organic Synapses for Neuromorphic Electronics: From Brain-Inspired Computing to Sensorimotor Nervetronics. *Acc. Chem. Res.* **2019**, *52* (4), 964–974.

(6) Paulsen, B. D.; Tybrandt, K.; Stavrinidou, E.; Rivnay, J. Organic Mixed Ionic–Electronic Conductors. *Nat. Mater.* **2020**, *19* (1), 13–26.

(7) E. Root, S.; Savagatrup, S.; D. Printz, A.; Rodriquez, D.; J. Lipomi, D. Mechanical Properties of Organic Semiconductors for Stretchable, Highly Flexible, and Mechanically Robust Electronics. *Chem. Rev.* **2017**, *117* (9), 6467–6499.

(8) Silverå Ejneby, M.; Jakešová, M.; Ferrero, J. J.; Migliaccio, L.; Sahalianov, I.; Zhao, Z.; Berggren, M.; Khodagholy, D.; Đerek, V.; Gelinas, J. N.; Głowacki, E. D. Chronic Electrical Stimulation of Peripheral Nerves via Deep-Red Light Transduced by an Implanted Organic Photocapacitor. *Nat. Biomed. Eng.* **2021**, DOI: 10.1038/s41551-021-00817-7.

(9) Fahlman, M.; Fabiano, S.; Gueskine, V.; Simon, D.; Berggren, M.; Crispin, X. Interfaces in Organic Electronics. *Nat. Rev. Mater.* **2019**, *4* (10), 627–650.

(10) Keene, S. T.; Lubrano, C.; Kazemzadeh, S.; Melianas, A.; Tuchman, Y.; Polino, G.; Scognamiglio, P.; Cinà, L.; Salleo, A.; van de Burgt, Y.; Santoro, F. A Biohybrid Synapse with Neurotransmitter-Mediated Plasticity. *Nat. Mater.* **2020**, *19* (9), 969–973.

(11) Torricelli, F.; Adrahtas, D. Z.; Bao, Z.; Berggren, M.; Biscarini, F.; Bonfiglio, A.; Bortolotti, C. A.; Frisbie, C. D.; Macchia, E.; Malliaras, G. G.; McCulloch, I.; Moser, M.; Nguyen, T.-Q.; Owens, R. M.; Salleo, A.; Spanu, A.; Torsi, L. Electrolyte-Gated Transistors for Enhanced Performance Bioelectronics. *Nat. Rev. Methods Prim.* **2021**, *1*, 66.

(12) Maya-Vetencourt, J. F.; Manfredi, G.; Mete, M.; Colombo, E.; Bramini, M.; Di Marco, S.; Shmal, D.; Mantero, G.; Dipalo, M.; Rocchi, A.; DiFrancesco, M. L.; Papaleo, E. D.; Russo, A.; Barsotti, J.; Eleftheriou, C.; Di Maria, F.; Cossu, V.; Piazza, F.; Emionite, L.; Ticconi, F.; Marini, C.; Sambuceti, G.; Pertile, G.; Lanzani, G.; Benfenati, F. Subretinally Injected Semiconducting Polymer Nanoparticles Rescue Vision in a Rat Model of Retinal Dystrophy. *Nat. Nanotechnol.* **2020**, *15* (8), 698–708.

(13) Krauhausen, I.; Koutsouras, D. A.; Melianas, A.; Keene, S. T.; Lieberth, K.; Ledanseur, H.; Sheelamanthula, R.; Giovannitti, A.; Torricelli, F.; Mcculloch, I.; Blom, P. W. M.; Salleo, A.; van de Burgt, Y.; Gkoupidenis, P. Organic Neuromorphic Electronics for Sensorimotor Integration and Learning in Robotics. *Sci. Adv.* **2021**, *7* (50), eabl5068.

(14) Ohayon, D.; Inal, S. Organic Bioelectronics: From Functional Materials to Next-Generation Devices and Power Sources. *Adv. Mater.* **2020**, *32* (36), 2001439.

(15) Ostroverkhova, O. Organic Optoelectronic Materials: Mechanisms and Applications. *Chem. Rev.* **2016**, *116*, 13279.

(16) Xu, J.; Wang, S.; Wang, G.-J. N.; Zhu, C.; Luo, S.; Jin, L.; Gu, X.; Chen, S.; Feig, V. R.; To, J. W. F.; Rondeau-Gagne, S.; Park, J.; Schroeder, B. C.; Lu, C.; Oh, J. Y.; Wang, Y.; Kim, Y.-H.; Yan, H.; Sinclair, R.; Zhou, D.; Xue, G.; Murmann, B.; Linder, C.; Cai, W.; Tok, J. B.-H.; Chung, J. W.; Bao, Z. Highly Stretchable Polymer Semiconductor Films through the Nanoconfinement Effect. *Science* **2017**, *355* (6320), 59–64.

(17) Lei, Y.; Deng, P.; Li, J.; Lin, M.; Zhu, F.; Ng, T.-W.; Lee, C.-S.; Ong, B. S. Solution-Processed Donor-Acceptor Polymer Nanowire Network Semiconductors For High-Performance Field-Effect Transistors. *Sci. Rep.* **2016**, *6* (1), 24476.

(18) Gumyusenge, A.; Tran, D. T.; Luo, X.; Pitch, G. M.; Zhao, Y.; Jenkins, K. A.; Dunn, T. J.; Ayzner, A. L.; Savoie, B. M.; Mei, J. Semiconducting Polymer Blends That Exhibit Stable Charge Transport at High Temperatures. *Science* **2018**, *362* (6419), 1131–1134.

(19) Gumyusenge, A.; Melianas, A.; Keene, S. T.; Salleo, A. Materials Strategies for Organic Neuromorphic Devices. *Annu. Rev. Mater. Res.* **2021**, *51* (1), 47–71.

(20) van de Burgt, Y.; Lubberman, E.; Fuller, E. J.; Keene, S. T.; Faria, G. C.; Agarwal, S.; Marinella, M. J.; Alec Talin, A.; Salleo, A. A Non-Volatile Organic Electrochemical Device as a Low-Voltage Artificial Synapse for Neuromorphic Computing. *Nat. Mater.* **2017**, *16* (4), 414–418.

(21) Steiger, C.; Abramson, A.; Nadeau, P.; Chandrakasan, A. P.; Langer, R.; Traverso, G. Ingestible Electronics for Diagnostics and Therapy. *Nat. Rev. Mater.* **2019**, *4* (2), 83–98.

https://doi.org/10.1021/accountsmr.2c00022
Acc. Mater. Res. 2022, 3, 669–671