SPINTRONICS

Dopants give organic electronics a new spin

Standfirst: Electron spins can travel long distances in heavily-doped organic materials.

Curt A. Richter and Emily G. Bittle

Organic electronics is thriving. Organic light-emitting diodes (OLEDs) can be found in products ranging from cell phone displays to high-end televisions, organic photovoltaics are close to being commercially viable, and even flexible organic electronic devices are on the horizon. Compared to conventional inorganic electronic materials, organic materials offer a number of advantages such as being light weight and mechanically flexible, which makes them ideal for flexible electronic applications [1,2]. Furthermore, synthetic chemistry techniques can be used to create molecules with specific electrical or optical properties. Organic, or plastic, electronic devices can also be fabricated by using inexpensive techniques such as roll-to-roll processing [3], which are cheaper and far less complex than the techniques used in the manufacturing of state-of-the-art silicon integrated circuits. As a result, organic electronics are typically only associated with relatively low-cost, large-area or disposable electronic applications, such as flat-panel displays, sensor arrays, smart cards, and radio-frequency identification (RFID) tags [4]. Writing in *Nature Electronics,* Deepak Venkateshvaran, Henning Sirringhaus and colleagues now show that certain organic materials also have fundamental properties that make them ideal for high-value spintronics applications [5].

Spintronic devices have a wide range of major applications, from magnetic field sensing and memory, to high-performance conventional and unconventional (such as neuromorphic) computing. Spintronics-based non-volatile magnetoresistive random-access memories (MRAMs) such as spin-transfer torque MRAM (STT-MRAM) are, for example, already commercialized. And looking ahead, properties including non-volatility and ultra-low power consumption, make spintronic devices one of the most promising approaches for overcoming the challenges associated with the scaling of current silicon-based integrated circuit technologies. Spintronic devices typically use both the charge and the quantum mechanical spin of the electrons in a semiconductor or a metal [6], but there are also devices that involve no conventional charge current and rely only on the transfer of spin currents to operate.

Organic semiconductors are expected to be ideal spin transport materials. Due to the low atomic number of carbon, as well as the other elements (such as hydrogen or oxygen) they are based on, organic materials have minimal spin–orbit coupling, which is the primary spin-flipping process in conventional inorganic metals and semiconductors. The organic materials are therefore expected to have very long electron spin coherence times and diffusion lengths,

making them prime candidates for use in spin transport devices. Experimental resonance techniques have also indicated that organic materials could have relatively long spin relaxation times [7].

The first experimental reports of spin injection into organic semiconductors appeared about 15 years ago [8, 9]. Since then, efforts to create novel organic spintronic devices have been growing rapidly. Unfortunately, reports on the spin properties of organic semiconductors vary and the reproducibility of published results remains an issue. A comprehensive theory of spin-polarized carrier injection and transport in organic semiconductors, which can explain such complex results, is also still lacking [10,11]. Venkateshvaran and colleagues – who are based at institutes in the UK, Germany, the US, and the Czech Republic – help clarify this situation by reporting conditions in which spin transport over long distances is possible in doped conjugated polymers. They show, in particular, that spin diffusion lengths of more than 1 μm are possible in these organic semiconductors.

Injecting spins into organic materials is challenging. Due to an effect known as impedance mismatch, the spin current into organic materials is strongly reduced at the interface between low-electrical resistance ferromagnetic materials and high resistance organic semiconductors. Venkateshvaran and colleagues overcome this technical hurdle by using a sophisticated spin-pumping technique. This technique is based on ferromagnetic resonance and can create pure spin currents without any accompanying charge current. When a junction between a ferromagnetic material (in this case, permalloy; Fig. 1) and a non-magnetic material (a doped organic polymer) is excited at the ferromagnetic resonance frequency, a spin-only current is injected into the non-magnetic material. The polarization of this spin current contains a small d.c. component, which can be detected as a voltage through the inverse spin Hall effect (ISHE) by using a metal (such as platinum) with a finite spin Hall effect. The spin diffusion length is then determined by measuring the ISHE voltage as a function of the distance between the permalloy “spin pump” and the platinum ISHE “detector”. The researchers carried out these experiments for an organic polymer known as F4TCNQ-doped PBTTT (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane in poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) and observed short transit times and the long spin diffusion lengths of more than 1 μm. They also observed comparable long spin diffusion lengths in other doped polymers such as P3HT and CDT-BTZ (poly(3-hexylthiophene-2,5-diyl) and cyclopentadithiophene-benzothiadiazole).

The long spin lengths are observed in organic polymers doped to very high concentrations of spin and charge carriers. In such high carrier-concentration materials, the spins are in close physical proximity and, as the researchers explain, spin-only currents can be readily transferred by a spin-exchange process. Venkateshvaran and colleagues compare these spin transport processes with those that occur in low-concentration organic semiconductors, where the spins are physically further apart and have weaker interactions. In the low-concentration regime, the

spins and charges are expected to move together. Charges in organic semiconductors typically move by a process of hopping from site to site, which leads to low carrier mobilities and short diffusion lengths. Therefore, spins are expected to have shorter spin diffusion lengths in this low-concentration spin and carrier hopping regime, which the researchers experimentally confirmed with lightly-doped organic polymers. The experimental results demonstrate that in the high spin concentration regime, organic semiconductors can have long spin diffusion lengths, even if the charge carriers have low mobilities and short scattering lengths. These insights may explain many of the experimental difficulties and short spin diffusion lengths reported in traditional measurements of spin in organic semiconductors, which are based on charge and spin currents.

The long spin diffusion lengths reported by Venkateshvaran and colleagues imply that organic semiconductors are an excellent spin transport media for cutting-edge organic spintronic devices. However, more work is needed to create viable organic spintronics technologies. To start, the researchers carried out their measurements by using specially-designed test structures in order to examine the fundamental properties of the organic materials and illustrate their potential in spin transport. Thus, it is critical to now use these materials in technologically-relevant spintronic devices and systems. Ultimately, organic materials could potentially be integrated with traditional digital complementary metal–oxide–semiconductor (CMOS) technology to create high-density, energy-efficient memories within digital central processing units. Hybrid organic spintronic and CMOS structures could perhaps even be used for future computing approaches such as standby-power-free, non-volatile CMOS logic and neuromorphic computing.

Curt Richter and Emily G. Bittle

Nanoscale Device Characterization Division of the Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland USA
e-mail: curt.richter@nist.gov

References

1. Qian, Y. et al. Adv. Mater. 28, 9243–9265 (2016).
2. Sirringhaus, H. Adv. Mater. 26, 1319–1335 (2014).
3. Tong, S. et al. npj Flexible Electron. 2, 7 (2018).
4. Gundlach, D. J. et al. Nat. Mater. 7, 216–221 (2008).
5. Wang, S.-J. et al. Nat. Electron. https://doi.org/10.1038/s41928-019-0222-5 (2019).
6. Ohno, H., Stiles, M. D. & Dieny, B. Proc. IEEE Inst. Electr. Electron. Eng. 104, 1782–1786 (2016).
7. Harris, C. B., Schlupp, R. L. & Schuch, H. Phys. Rev. Lett. 30, 1019–1022 (1973).
8. Dediu, V. et al. Solid State Commun. 122, 181–184 (2002).
9. Xiong, Z. H., Wu, D., Vardeny, Z. V. & Shi, J. Nature 427, 821–824 (2004).

10. Jang, H.-J. & Richter, C. A. Adv. Mater. 29, 1602739 (2017).
11. Dediu, V. A., Hueso, L. E., Bergenti, I. & Taliani, C. Nat. Mater. 8, 707–716 (2009).

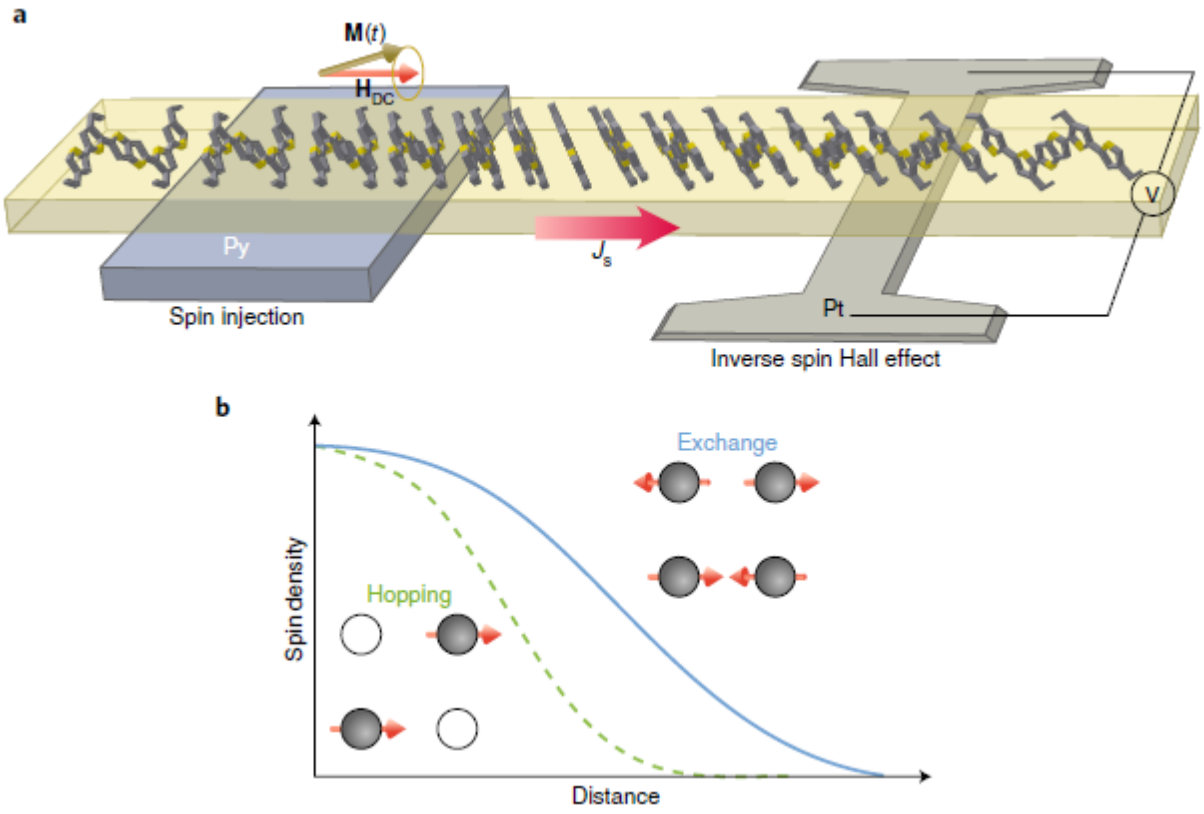

Fig. 1. Lateral spin pumping and detection. **a**, Pure spin current is injected at the interface between the permalloy (Py) and the organic semiconductor. The spins are detected as a voltage by the inverse spin Hall effect in the platinum (Pt). Doped polymers mediate the spin movement. The red arrow denotes the externally applied magnetic field, H_{DC}.The gold arrow illustrates the dynamic magnetization, M(t), precessing around H_{DC}. **b**, Venkateshvaran and colleagues suggest that a likely mechanism for the spin current (J_S) in heavily doped polymers is diffusion through the polymer by spin-exchange, rather than coupled charge–spin hopping through the material. This leads to large (around 1 µm) spin diffusion lengths, despite low charge mobility. Credit: panel **a** adapted from ref. 5, Springer Nature Ltd.