particular models to be clarified and recognized, and provide predictions that are experimentally falsifiable.

Additionally, only recently have quantum chemists developed the capabilities to simulate transport properties on the scale of individual molecules⁵. Although simulating true bulk materials is not yet possible, a bottom-up approach has the potential to provide the most complete and satisfying theoretical description of organic electronic and spintronic devices, especially those aspects with no direct analogies in inorganic semiconductors, such as chemical substitution and morphology⁶. Fortunately, the chemical tunability of organic materials allow for near direct control over the material properties that influence spin. This provides, in our view, a strong way to experimentally test models describing spins in organic semiconductors⁷, and indeed for more fundamental studies of spin interactions with the environment⁸.

A similarly unified approach should also be extended to model testing. We note the breadth of expertise required to develop traditional inorganic materials and devices, particularly during the early years of these technologies⁹. Similarly, a proper scrutiny

of unified models for spins in organic materials will require the interdisciplinary work of researchers across condensed matter and quantum physics; physical, organic and synthetic chemistry; device design and engineering; and materials and device characterization.

Although we agree with Boehme and Lupton that spin-based spectroscopy is a powerful method for investigating spins in organic semiconductors, we feel that any and all informative characterization techniques should be used. We stress, however, that care needs to be taken to ensure that the subtleties inherent in applying complex characterization techniques to organic semiconductors are well thought through. For example, assumptions underlying our interpretation of conventional spin-based spectroscopic techniques applied to organic semiconductors are being challenged¹⁰. Similar issues could easily lead to erroneous interpretation of other techniques, if not promptly identified.

The empirically led development of the field has promoted ambiguity in models and definitions that now abound. Magnetoresistance measurements alone have proven insufficient to distinguish these models, and it is now time to draw

on the expertise of other fields. We need to expand the repertoire of characterization techniques we use to scrutinize spins in organic semiconductors. We must then use the results of these measurements to test unified, falsifiable, predictive theories that will drive the development of spin-based organic devices. □

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Is there more than meets the eye?

To the Editor — I fully support the call of Boehme and Lupton¹ to use basic spectroscopy to untangle spin-dependent phenomena in organic semiconductors as well as to have a minimalistic approach to modelling. However, I would like to add a call for logical reasoning, which is an equally important ingredient of fruitful science. By also giving logical reasoning weight, some of the views held by Boehme and Lupton should be adjusted. I give two examples.

First, I agree that electron–hole polaron-pairs are likely to play an important role in the magnetic field effects observed in bipolar organic devices, as strong spectroscopic evidence — provided for a large part by the groups of Boehme and Lupton — suggests. However, the polaron-pair model is not sufficient to explain bipolar organic magnetoresistance, as this would require a significant probability for unbinding of a polaron pair as compared with the probability for exciton generation. A simple estimate yields a polaron-pair binding energy of about 0.5 eV, that is, about 20 kT at room temperature. Therefore, the logical conclusion is that it is unlikely that unbinding of a polaron pair can compete

with the energetically favourable process of exciton formation. Although maybe difficult to demonstrate spectroscopically and not minimalistic, the idea — not addressed by Boehme and Lupton — that bipolar magnetoresistance is caused by the interaction of charges with a magnetic field-dependent number of long-lived triplet excitons² would solve the problem.

The second example concerns their view of the bipolaron model as an unlikely explanation for organic magnetoresistance in unipolar devices, because a ‘possibly unrealistic’ structural relaxation of the order of 10 kT at room temperature would be needed to stabilize bipolarons. Simulations with realistic parameters have shown that stabilization of bipolarons is not required for an explanation of organic magnetoresistance³. This is because bipolarons can be present as (short-lived) transient states necessary for transport along the quasi-one-dimensional current pathways formed by disorder-induced percolation³. The view that bipolarons can play a dominant role in unipolar magnetoresistance is supported by the observation of an extremely large

magnetoresistance in strictly one-dimensional molecular wires⁴. Logical reasoning excludes the polaron-pair model in this case: the largest magnetoresistance occurs at voltages that are too low to generate electron–hole pairs.

These examples show that the call of Boehme and Lupton is too restricted. I do support their call to provide spectroscopic proof for suggested physical mechanisms, however, this could be far from easy in some cases: the presence of short-lived transient bipolaron states may be very difficult to observe spectroscopically. There may be more than meets the eye and room should also be given to logical reasoning. □

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