

SIMULATING “SOFT” ELECTRONIC DEVICES

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ABSTRACT

A combination of classical molecular dynamics simulations and very large scale semiempirical molecular orbital calculations has been used to simulate field-effect transistors in which both the dielectric layer and the semiconductor are incorporated in a self-assembled monolayer of suitable functionalized alkylphosphonic acids. In such simulations, both the dynamics of the flexible organic molecules and the electronic properties of the molecular aggregates must be taken into account. First steps towards realistic simulations of such devices are described.

INTRODUCTION

Modeling and simulation of molecules and molecular aggregates requires that two aspects of the modeling task be treated adequately; the Hamiltonian(s) used to describe the system and the conformational sampling. Whereas conformational sampling only plays a small role in many cases in which small molecules are modeled, it becomes the dominant aspect of modeling macromolecules, so that the quality of the Hamiltonian is dictated by the need for extensive sampling. This is generally not a problem as modern force fields provide

adequate energy hypersurfaces at very reasonable computational cost, so that in particular biopolymers can be simulated for several microseconds on specialized hardware [1]. Such classical molecular-dynamics (MD) techniques have become essential in biological and medicinal research, but are of limited use in simulating organic electronics devices because they treat the electrons implicitly in what is essentially a coarse-grained ansatz designed to mimic quantum mechanics. It is therefore necessary either to perform direct quantum mechanical MD (e.g. Car-Parinello density-functional theory (DFT) based MD) or to use a multiscale treatment in which the MD (i.e. the conformational sampling) is performed classically and the geometries of “snapshots” from the classical MD-simulation used for hundreds or thousands of single-point quantum mechanical calculations to determine the electronic properties. Because the classical simulation typically treats tens of thousands of atoms, the “snapshots” are very large for quantum mechanical treatments. This means that either only the most interesting components of the snapshot (e.g. the chromophores [2]) are treated quantum mechanically in a hybrid quantum mechanics/molecular mechanics (QM/MM [3]) approach or that very large scale quantum mechanical calculations must be used. This limits the choice of technique available. Linear scaling *ab initio* [4], or DFT [5] calculations are able to treat thousands of atoms, but not yet to perform calculations on thousands of snapshots, each consisting of tens of thousands of atoms. This means that “cheaper” quantum mechanical methods such as semiempirical molecular orbital (MO) theory [6] or tight-binding-based DFT [7] must be used. Because the self-interaction error limits the usefulness of DFT-based techniques for applications in which electrons are transferred from one moiety or region to another, [8] semiempirical MO-theory is our method of choice.

Linear scaling versions of semiempirical MO theory are usually based on the divide-and-conquer (D&C) [9,10] or localized molecular orbital (LMO) [11] techniques. However, because these both use local approximations, they are not suitable for electronics applications in which conjugation over large distances, areas and volumes is important. This is simply because the long-range interactions that determine the characteristics of extensively conjugated systems are explicitly excluded from local approximations because they can be neglected in non-conjugated systems. This means that full semiempirical self-consistent field (SCF) calculations must be performed. However, these scale with N^2 to N^3 , depending on the implementation, so that very large-scale calculations rapidly become prohibitively expensive. In this article, we describe our simulations of field-effect transistors (FETs) constructed using self-assembled monolayers (SAMs) of organic molecules as an example of the challenges of such applications and the strategies that can be used to overcome them.

THE SAMFETs

The self-assembled monolayer field-effect transistors (SAMFETs) consist of gold source and drain electrodes, an oxidized aluminum drain electrode and a multifunctional SAM that provides both the insulating dielectric and the semiconductor layers [12]. Figure 1 shows a schematic view of a typical SAMFET.

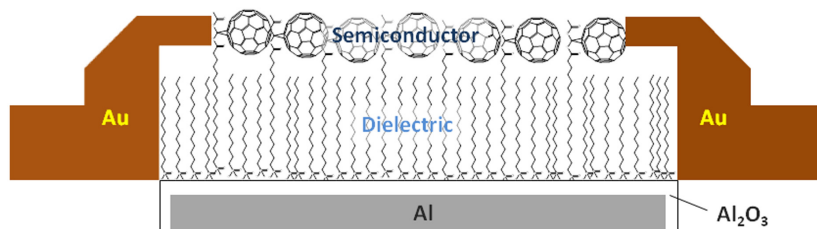


Figure 1. Schematic and idealized view of a SAMFET with an n-type semiconductor layer consisting of fullerene moieties.

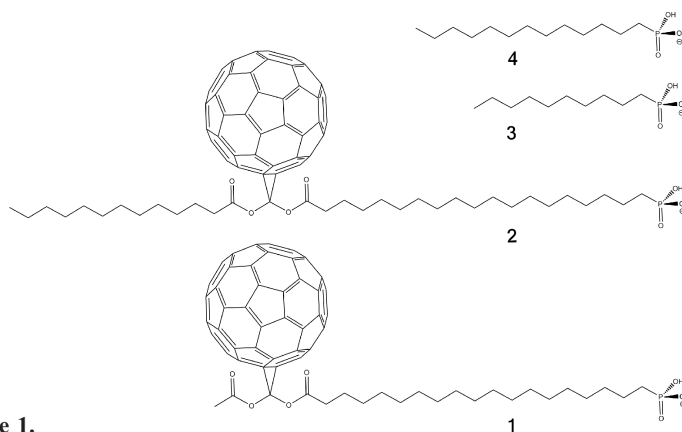
The first important point illustrated in figure 1 is that the schematic view of the SAM is idealized in the extreme. The alkane chains do not all align in an orderly fashion perpendicular to the Al_2O_3 surface; the SAM is a dynamic and only moderately ordered structure. Similarly, the orderly row of fullerenes that act as the semiconductor is an ideal situation that is unlikely to be realized in a real device. An important point is that the SAM consists of a fullerene-functionalized molecule and one with a pure alkane tail. It was found experimentally that mixtures of such compounds gave functioning SAMFETs, whereas a SAM consisting of only fullerene-substituted molecules give only very poor transistor-like characteristics with very high gate currents. The interpretation shown in figure 1 that the unsubstituted molecules form a cushioning layer below the fullerenes is simply a rationalization of these experimental results. Figure 1 shows a fullerene-substituted SAM, which gives an n-type semiconductor layer. As an alternative to the fullerenes, oligothiophenes can be used to give a p-type semiconductor layer [13].

Rational design of SAMFETs of this type requires detailed knowledge at the atomistic level of the structure and electronic properties of the SAMs. This information is difficult to obtain experimentally, so that simulations provide a valuable source of information. This is true of purely classical simulations of the dynamic structure of the SAMs but even more so if electronic properties can also be calculated. This combination of structural dynamics and electronic properties represents a computational challenge that is only now becoming accessible because of the constant improvement in both hard- and software. In the following, we describe some aspects of this challenge and the techniques developed so far to answer it.

STRUCTURE OF THE SAMs: CLASSICAL MOLECULAR DYNAMICS

The MD simulations of SAMs used the 0001 surface of Al_2O_3 to represent the oxidized surface of the aluminum gate electrode. The 52×38 nm Al_2O_3 slab (five layers) was first equilibrated in the gas phase and then held fixed during the SAM simulations. One potential difficulty in such simulations is the treatment of the bonding between the Al_2O_3 and the organic molecules that make up the SAM. The alternatives are to define classical “covalent” bond potentials (in reality quadratic potentials according to Hooke’s law) that cannot be broken or to treat the interaction as purely electrostatic. The latter alternative has the advantage that the organic molecules can dissociate from the surface or rearrange, so that for instance the surface coverage can adjust to an equilibrium value. Purely electrostatic binding was therefore used in the simulations. The Generalized Amber Force Field (GAFF [14]) was used for the organic molecules.

The SAMs consisting of anions **1** – **4** were constructed as regular arrays on the Al_2O_3 surface and allowed to equilibrate. Some molecules dissociated from the surface but stable SAMs were obtained in all simulations.



Scheme 1.

The simulations confirmed the main thrust of the interpretation shown schematically in figure 1 but also revealed details not accessible otherwise. Figure 2 shows a snapshot from an equilibrated simulation using a SAM consisting of pure **1**. The surface coverage is fairly low (0.9 molecules nm^{-2}) and the fullerenes do not form a single layer, but are rather distributed at different levels above the Al_2O_3 surface. More importantly, in this simulation individual fullerenes already contact the Al_2O_3 surface during the warm up phase (starting from an ordered vertical SAM). Further surface contacts are made within 20 ns simulation time. Snapshot showing one such occurrence is shown in figure 2.

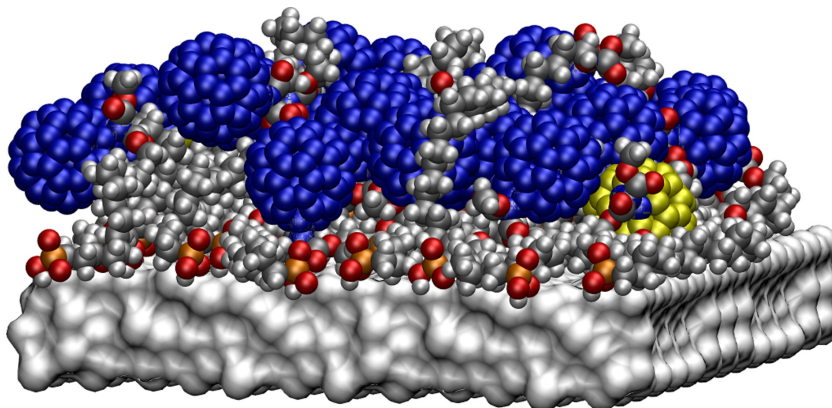


Figure 2. Snapshot taken from a simulation of a SAM consisting of pure **1** after 50 ns. The fullerene moiety that contacts the Al₂O₃ surface is colored yellow.

The simulation using a mixed SAM (25% **1**, 75% **3**) behaves differently. The initially perpendicular SAM adopts an average angle to the Al₂O₃ surface of approximately 58° after approximately 10 ns and remains at this angle throughout the remaining simulation time. More importantly, the fullerene moieties remain separated from the Al₂O₃ surface by a closed and consistent layer of alkyl chains, as shown in a representative snapshot (Fig. 3).

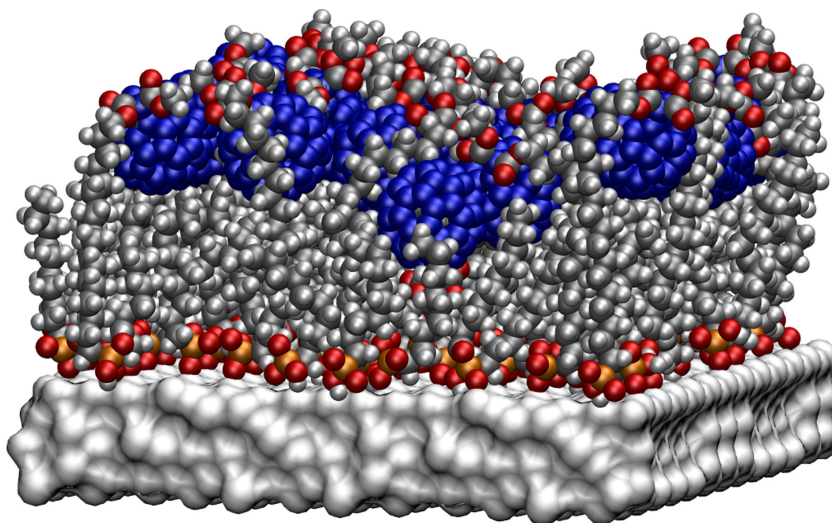


Figure 3. Snapshot taken from a simulation of a SAM consisting of 25% **1** and 75% **3** after 50 ns. The fullerene moieties form a defined layer.

This behavior is completely consistent with the experimental observations. A simple optical analysis of the simulation shows that the alkyl chains remain as a moderately ordered continuous layer below the fullerenes, which form a second fairly regular layer above them. This is the configuration required for the SAM to act as an FET. However, the classical simulations do not allow us to analyze the electronic properties of the SAM.

VERY LARGE SCALE SEMIEMPIRICAL MO CALCULATIONS

Modern NDDO-based semiempirical MO-calculations are almost exclusively derived from the original MNDO technique. [6, 15, 16] As discussed above, linear scaling techniques that rely on local approximations [9, 10, 11] are not suitable for extensively conjugated systems, so that software is needed that performs the full NDDO-based SCF calculation on many thousands of atoms. This and the current hardware emphasis on multi-core architectures mean that a highly parallel program is necessary. Unfortunately, little emphasis has been placed on parallel semiempirical MO codes, probably because the major computational task is the diagonalization of the Fock matrix. Matrix diagonalizations perform relatively poorly on highly parallel architectures.

We therefore conceived the EMPIRE program, [17] to perform very large (designed for up to 50,000 atoms, tested up to 100,000) on massively parallel (designed and tested up to 1,024 processors) compute clusters. Because the diagonalization of the Fock matrix represents the major bottleneck in the parallel calculation, the SCF iterations were designed to proceed with as few diagonalizations as possible. The details of the implementation have been reported elsewhere but the major design considerations were as follows:

- Memory requirements increase with N^2 , where N is the number of atomic orbitals. Memory requirements were therefore reduced to a minimum. Ideally, only four $N \times N$ matrices are used.
- Memory access is slow relative to floating-point calculations, so that most quantities required during the calculation (e.g. two-electron integrals, the one-electron matrix) are calculated on the fly. The one-electron matrix can optionally be stored and reused in every SCF cycle.
- A hybrid parallelization strategy (openMP within a node, MPI between nodes) was used to optimize performance.
- The calculations rely heavily on Intel's optimized MKL parallel library for the majority of calculations within one node.
- The important matrices are distributed across the compute nodes in stripes to minimize communication.

An important component of the EMPIRE program is an accurate initial guess (the starting set of molecular orbitals for the SCF iterations) that allows it to converge for most systems very quickly without need for convergence accelerators, which generally require copies of past density matrices to be stored. The program was used to calculate 150 snapshots from each MD simulation in order to be able to estimate the electronic properties of the SAMs. Because periodic calculations are not yet possible, one simulation box without its Al_2O_3 slab was used for the snapshots, resulting in calculations for approximately 6,000 atoms.

ELECTRONIC PROPERTIES

One practical difficulty with MO calculations on many thousands of atoms is that the traditional analysis techniques (population analyses, individual MOs etc.) rapidly become too cumbersome for very large numbers of atoms. A more easily understood (and less space-demanding) technique is to calculate the values of informative local properties. The best known local properties are the electron density, which is usually used to construct an isodensity molecular surface [18] and the molecular electrostatic potential (MEP), [19] which indicates possible hot spots for Coulomb interactions. Local equivalents of the donor and acceptor levels are the local average ionization energy [20] and the local electron affinity, EA_L . [21, 22] These quantities are in essence density-weighted Koopmans theorem [23] ionization potential and electron affinity, respectively. An extensive review of local properties was given in an earlier article in this series [24].

For an n-type semiconductor, the most informative of these local properties is EA_L because it corresponds approximately to the acceptor level of the semiconductor and gives an easily understandable picture of electron transport in molecules and aggregates [25]. This technique allows us to visualize the space-resolved acceptor characteristics of the SAMs, as shown in figure 4.

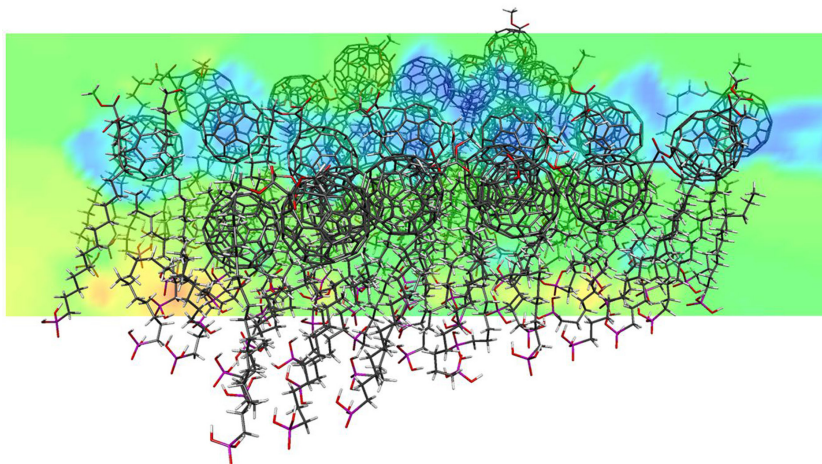


Figure 4. The local electron affinity (calculated using the AM1 Hamiltonian) for a diagonal vertical plane through a snapshot from the simulation illustrated in figure 2. The color coding runs from blue (most positive) to red (most negative). Electron affinities are defined as the ionization potential of the reduced species, so that the blue areas are those that accept electrons most readily.

Figure 4 shows a clear almost continuous blue band through the fullerene layer that indicates an almost uninterrupted path for electron transport through the upper layer of the SAM. However, this is only one snapshot. A complete analysis of the behavior of the device would

require that the time-dependent behavior be analyzed using as many snapshots as possible from as long a simulation as possible. This is clearly not possible by visual inspection, so that more quantitative analysis techniques must be used.

ELECTRON-TRANSFER PATHS

Electron-transfer paths were determined by a simple Monte-Carlo procedure. “Electrons” (in reality simply points that are assigned the local electron affinity at their position as energy function) are subjected to a Metropolis Monte-Carlo procedure in which they are only allowed to move from the source towards the drain, not in the reverse direction. Performing many such simulations at different temperatures leads to many paths that do not cross to the drain (shown in blue in figure 5) and some “conducting paths (shown in gold) that reach the drain. Figure 5 shows the results of such simulations at $kT = 215$ mV.

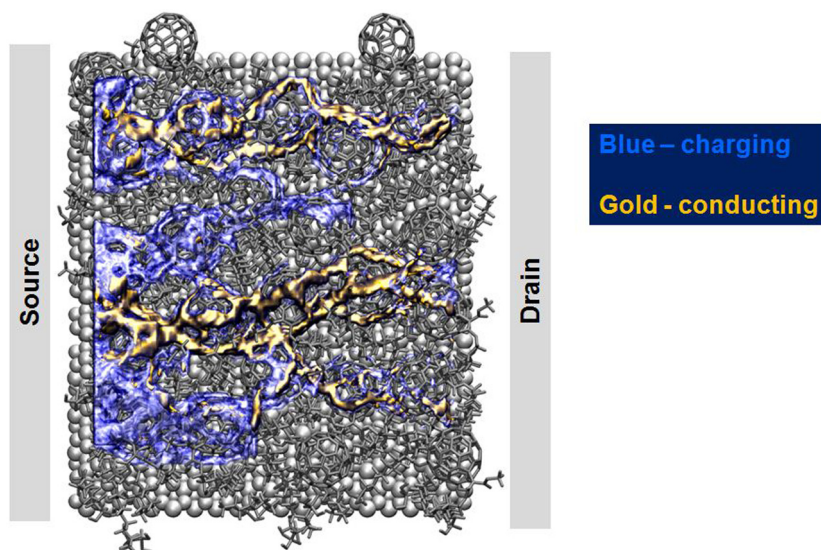


Figure 5. Electron-transfer paths through a snapshot of the mixed SAM. Blue paths are those that terminate in the SAM (and would therefore lead to accumulation of negative charge) and those in gold reach the drain electrode. The “source” and “drain” are in reality a little inside the edges of the SAM, as can be seen from the origins and ends of the paths. The Monte-Carlo simulation was carried out at $kT = 215$ mV.

The effect of the Monte-Carlo temperature on the paths can be seen in figure 6.

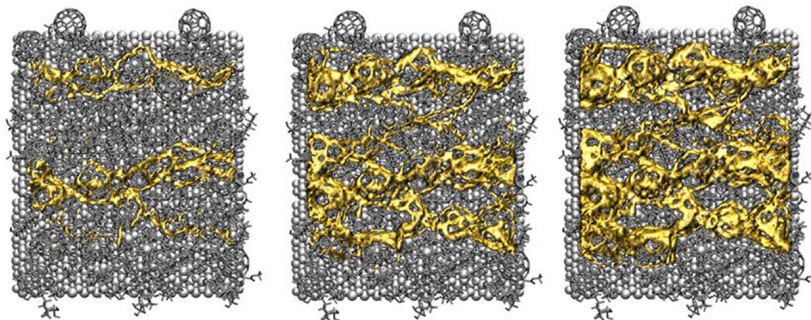


Figure 6. Electron-transfer paths through a snapshot of the mixed SAM at different “electronic” temperatures ($kT = 215$, 285 and 308 mV from left to right, respectively). The “source” and “drain” are in reality a little inside the edges of the SAM, as can be seen from the origins and ends of the paths.

The three sets of paths were found for the same MD snapshot at an “electronic” (= Monte Carlo) temperature of $kT = 215$, 285 and 308 mV from left to right, respectively. The paths shown in the left-hand ($kT = 215$ mV) plot correspond to the conducting paths shown in Figure 5. As expected, increasing the “electronic” temperature (applied voltage) increases the number and cross sections of the “conducting” paths.

The paths shown in figure 5 are informative but at the moment do not take two factors into account. These are once more the conformational sampling, which would mean that hundreds or thousands of such simulations on different MD snapshots must be performed, and the fact that the “electrons” are uncharged and do not interact with each other.

“CONDUCTANCE” SIMULATIONS

A next step towards more realistic simulations of conductance in the SAMs is to include electron-electron interactions as point-charge Coulomb energies to be added to the local electron affinity. This is a very coarse approximation, but at least introduces the effect of electrons bound in the semiconductor layer. Figure 7 shows the results of one such simulation in which electrons are fed into the SAM from the source at a constant rate and removed from the simulation as soon as they reach the drain. The figure shows the situation after the simulation has come to equilibrium.

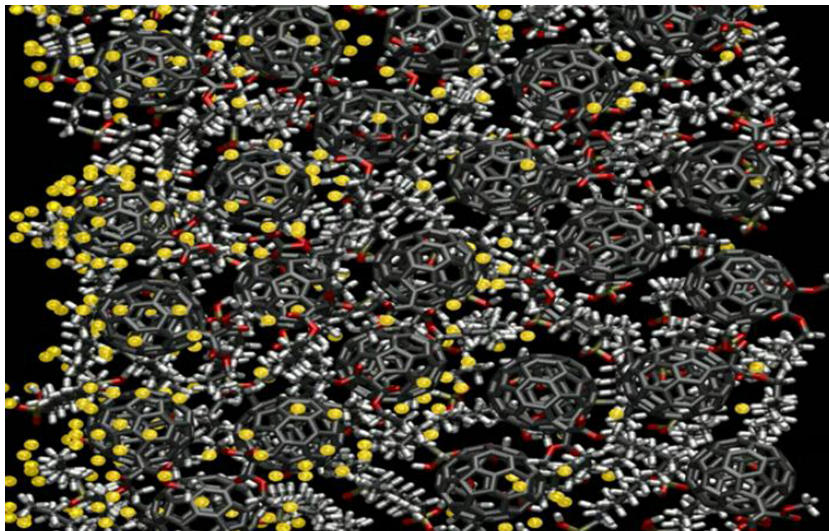


Figure 7. Snapshot of a Monte-Carlo simulation of conductance of classical point-charge electrons through the SAM. The electrons are shown as yellow balls and are free to move in all directions. The placing of the “electrodes” is the SAM as in figures 5 and 6.

Although the physical model used in the simulation is clearly not yet realistic, several features are in accord with our expectations. A potential across the SAM layer is built up by trapping electrons close to the source until the driving force provided by the electrostatic repulsion is sufficient to force the front-line electrons across the semiconductor layer to the drain. Once this potential has been built up, the simulation reaches a steady state in which electrons injected at the source result in others being removed at the drain. This model is also able to introduce a substantial negative charge into the semiconductor layer. Experiments suggest that this does indeed happen in fullerene-based SAMFETs and that the charge accumulation leads to significant hysteresis in the I/V curve. [12, 26] Even this very simple simulation suggests that the inter-fullerene van-der-Waals contacts serve as electron traps and that electrons are also trapped on the surfaces of the fullerene moieties. The latter is expected, but the high stability of electrons trapped between fullerenes was unexpected and is now being investigated using more sophisticated calculations.

SUMMARY AND OUTLOOK

The simulations described above are only the beginning. The model used for electron transport is primitive in the extreme and quantitative predictions of device characteristics such as I/V curves are not yet possible. Several significant effects must still be considered:

- The Monte-Carlo simulations have so far been performed on a single, static SAM-structure. Realistic simulations must couple the two time scales of atomic and electronic movement.
- The electrons have so far been treated as classical point charges. In reality, their traps are delocalized over a finite volume.
- Movements over barriers have also been treated classically. In reality, tunneling between the traps must be treated adequately.
- Perhaps the most difficult problem at the moment is to treat the interactions between the fullerenes in the presence of excess electrons correctly in the MD simulations. Reduced fullerenes do not always repel each other as they do in our classical model and may even form a covalent fullerene radical anion dimer [27]. These interactions must be taken into account, which is most easily achieved using direct QM/MM simulations, which will be computationally very expensive.

Nevertheless, much progress has been made in a research area for which conventional simulation techniques are often no longer adequate. Above all, the questions posed by the research goals must be answered by pushing existing techniques to their limits and making optimal use of computing facilities. This type of interdisciplinary research-driven method development over different time and length scales represents an important new direction in modern modeling and simulation.

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