Advancing organic optoelectronics with charge transfer nanocomposites

Within the last ten years, astonishing advances have been made in electro-active organic materials for applications such as organic emissive devices, transparent conducting coatings, organic sensors, and optical switches. However, the development of organics for use in these technologies is still faced with significant challenges. In fact, quantification of optical-field-coupling mechanisms and the systematic description of transport are still far from being realized in conjugated systems; though the framework for such understanding has already been established. What has become clear is that full realization of conducting polymers in high-performance applications will require novel approaches beyond traditional chemical-doping schemes.

There are countless examples of applications that are ‘just missed’: one of which is photovoltaics. Organics are quite good at converting photons into excitons, but it is nearly impossible to remove substantial amounts of these excitations from a polymer layer as a useful current. The difficulty comes from a fundamental mismatch of length scales: migration lengths for the donor-acceptor excitations (50nm) are much shorter than the absorption lengths required to create the excitations (500nm). Clearly, it would be useful to engineer optical and electronic phenomena by linking relevant length scales, thus altering the coupling between polymer excitations and photon fields. In fact, this seems to be possible with blends of conjugated polymers and dispersed, single-walled carbon nanotubes (SWNTs). Subtly different in concept from polymer-polymer blends, these ‘charge-transfer-nanocomposites’ (CTNs), as they have come to be called, can express remarkable electronic conduction, photo-emissive, and photo-absorption properties. While fullerenes and their derivatives (such as SWNTs) were among the first examples, these concepts have now been extended to include any engineered nanophase dispersed into the electro-active polymer matrix.

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Figure 1. To demonstrate how these novel composites could be integrated into display pixel technology without significant degradation to performance, we used indium tin oxide (ITO), poly-3,4-ethylenedioxythiophene (PEDOT), and poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene (PmPV), with single-walled nanotubes and aluminum tris(8-hydroxyquinoline) (Alq3), plus nile red/AlLiF. Notice the pixel can be shifted between green poly(p-phenylene vinylene) (PPV) and red (NR-doped Alq3) by changing the driving voltage.

Figure 2. Nanocomposite devices are far more efficient than pure PPV devices: PPV and PPV+C60 devices are compared here. The percolation threshold is 3% loading.
trix to create a family of CTNs.

There have already been a number of surprising demonstrations of technology based on CTNs. Among the most striking is one showing control over the recombination region in an organic light-emitting diode (OLED). By using CTNs, shallow trapping states are introduced into the emissive matrix that exhibit field dependent de-trapping. This results in a narrow recombination zone with a field-dependent position within the structure. When used in multilayered OLED structures, CTNs allow the construction of dynamic, multicolored, pixels as seen in Figure 1.

It has been known for some time that the nanoparticle (C₆₀, SWNT, etc.) dispersant, or the nanophase, introduces a discrete donor-acceptor state within the HOMO-LUMO gap (the gap between the highest occupied molecular orbit and the lowest) of the polymer host. The next most natural step is to engineer the position of this state within the band gap. Then, one might argue that a greater range of properties could be tapped. In fact, this can be seen using standard thin film OLED structures with fullerene (C₆₀) based CTNs. As mentioned above, these have long been studied for their potential in photovoltaic applications. This implies luminescence quenching would be associated with such a CTN, due to dissociation of the excitons through resonant energy transfer of the electron to the nanophase. However—when the emissive polymer is chosen such that the fullerene levels fall outside of the polymer band gap—an unusual enhancement in luminosity of the CTN device is observed (when compared with the pure polymer devices). As seen in Figure 2, this enhancement can be significant. Further, OLED structures using carbon nanotube-based CTNs have now been shown to be compatible with a number of lithographic techniques as seen in Figure 3.

When the nanophase-polymer system is chosen such that the nanoparticle trapping state falls within the HOMO-LUMO gap of the host, then the donor-acceptor behavior of the CTN is ideal for bulk heterojunction formation in photovoltaic applications. C₆₀ bulk-heterojunction organic photovoltaics are currently being investigated by a number of groups. Unfortunately, charge removal requires hopping conduction throughout the nanophase, raising the internal resistance of the device and lowering the overall external efficiency. An interesting solution to this predicament was recently attempted using carbon nanotubes. In this case the nanotubes form high-mobility pathways out of the device. Unfortunately, this approach has also has a difficulty: holes are typically transferred onto the nanotubes and the electrons have low mobility. Again, engineering the donor-acceptor state by modifying the energetics of the nanotubes would be ideal. Recently, we have demonstrated the ability to substitute dopant atoms into the lattice of carbon nanotubes, allowing us to adjust their overall electron affinities.

At this point, little is known quantitatively about the interaction between polymers and nanoscale materials such as carbon nanotubes. However, the potential impact of CTNs on organic devices is tremendous. Indeed, preliminary evidence suggests that they may be a significant step forward in electro-active polymer technologies.

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Figure 3. A Wake Forest University Seal organic light-emitting diode (OLED) made from nanocomposites. The structure was patterned using standard UV lithography techniques. The smallest line width of the structure is approximately 100 µm.

References
Enzymes as molecular motors

Type I restriction-modification (R-M) enzymes are multifunctional, contain multiple subunits, and provide bacteria with protection against infection by DNA-based bacteriophages: for a recent review see Reference 1. They accomplish this through a complex activity that cleaves the DNA at random locations that can be far away (>20 kilo base pairs, kbp) from the enzyme’s recognition sequence or usual specified cleavage site. The R-M enzyme has a powerful ATPase activity: that is, it is good at converting adenosine triphosphate (ATP) into its diphosphate (AD). This conversion process is associated with DNA translocation (involving the exchange or re-arrangement of segments) before cleavage, and thus to the production of random cleavage sites. These enzymes are, therefore, unusual molecular motors: they bind specifically to sections of DNA and then move the remainder through this bound complex (see Figure 1).

The enzyme we are using in our studies (see Figure 2) is EcoR124I, from the type-IC R-M family. The fully-functional R-M enzyme comprises three subunits (HsdR, M, S) in a stoichiometric ratio of R₂M₂S. However, Janscák et al. also showed that the EcoR124I R-M holoenzyme exists in equilibrium with a sub-assembly complex of stoichiometry R₁M₂S, which is unable to cleave DNA, but retains the ATPase and motor activity. Therefore, we have available a motor that can translocate DNA without cleaving it.

A useful molecular motor

The majority of DNA-based molecular motors are ‘linear-tracking’: they can be likened to railway trains running along railway tracks. These use the repetitive nature of the DNA sequence to enable them to move along the molecule. The best example, and one of the most closely studied at the single-molecule level, is RNA (ribonucleic acid) polymerase. In single-molecule studies of this motor, optical tweezers were used to hold a polystyrene bead attached to the DNA, while the motor was attached to a surface.

Type I R-M enzymes, on the other hand, are unusual as molecular motors: the enzyme binds to a specific site on the DNA strand and remains bound at that site while moving the adjacent section and so acting as a nano-actuator (see Figure 2). It can be likened to the spool of a fishing rod, where the line is the DNA. This means that a useful device can be constructed without the motors being directly attached to the surface: the DNA can be attached instead (see Figure 3).

DNA translocation by Type I R-M enzymes was assayed (quantified) in bulk solution using protein-directed displacement of a DNA triplex: we determined a translocation velocity of 400±32bp/s at 20°C. The data showed a bi-directional translocation for the R₁ complex and, importantly, the R₂ complex could still catalyze translocation in a single direction. The latter reaction is less processive, but can ‘reset’ to either direction whenever the DNA is released.

Thus, we have a molecular motor that binds to a DNA molecule and pulls the end of the strand toward it. The DNA can easily be surface-attached, producing a nanoactuator, and a wide variety of ligands or objects can be attached to the other end of the molecule to allow easy detection of movement (see Figure 4). In our recent studies, a magnetic bead is attached to the distal end of the DNA and a magnetic-tweezer setup is used to measure translocation. We have determined the rate of translocation for single molecules and the ATP-Continues on next page.
dependence of the motion.8

Potential use of the motor
By definition, the motor is a nanoactuator. As part of a EU-funded 5th Framework Research and Development Project, we are developing a molecular magnetic switch that links the biological and silicon worlds (Mol Switch). This project set out to produce a biological molecular motor that could ‘pull’ a ‘string’ through itself, acting as a nanoactuator: and we have succeeded in producing such a device. Attached to one end of the ‘string’ was a magnetic bead, whose movement could easily be detected and which acted as a molecular dynamo. The ‘string’ used was DNA (a nanometer-wide thread), to which the bead was easily attached (a routine procedure in molecular biology). We are currently developing a self-assembly process to build the nano-actuator on a silicon surface.

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Figure 4. The ‘Mol Switch’ device: a Hall-effect sensor generates electrons as the magnetic bead rotates. The current produced can be used to drive electronic devices, thus linking the biological and silicon worlds.
Nanotechnology to go: active transport by motor proteins

Central technologies in the macroscopic world involve the transport and manipulation of objects: either over long distances—using railways, ships, or planes—or over short distances, as in an assembly line. In nanotechnology, we can often rely on diffusion to move molecules and nanoscale objects into position or transport them over short distances, but active transport under user-control is mostly limited to pushing objects around with the tip of a scanning-probe microscope. In contrast, cells use a large number of specialized motor proteins to distribute specific molecules and organelles to defined locations. These nanoscale transporters permit cells to achieve non-uniform distributions of molecules, to greatly accelerate the delivery of critical building blocks, and to actively reorganize their internal structure in response to external stimuli. Taking advantage of these attributes would be very desirable in micro- and nanoscale devices, however, current molecular-scale synthetic motors do not yet achieve the functionality of their biological counterparts.

To explore the full potential of active transport on the nanoscale, we are pursuing a hybrid approach employing biological motors integrated into synthetic elements, such as microfabricated devices. A focus of our research is the design of a motor-protein-based ‘molecular shuttle’, which is capable of transporting molecular-sized cargo along predetermined tracks under user control. Such a nanoscale transport system could then serve as a module in a nanoscale assembly line, as a means of transporting analytes in a biosensor, or as a component of an adaptive material.

One possible task by which motor proteins can add completely new attributes to microfluidic devices is sketched in Figure 1. Kinesin motor proteins have a cargo-binding tail and two feet to bind specifically to, and walk along, microtubules: the latter are tubular assemblies of the protein tubulin with a diameter of 24nm. The kinesin motors are tethered to the surface by their tails and, in the presence of ATP (adenosine triphosphate, the energy source) the motors can bind to the microtubules and move them along. The microtubules can be functionalized with specific linkers, such as biotin, to permit selective loading of cargo. Different surface modification approaches have been developed to effectively guide the movement of microtubules in complex networks of micron-scale tracks (see Figure 2).

A wide range of optical techniques can be used to interact with these shuttles. Most importantly, fluorescence microscopy is an ideal tool to determine the position of molecular shuttles by detecting the fluorescence of dyes or quantum nanodots linked to the microtubules. While fluorescence microscopy permits the observation of multiple shuttles moving in a large field-of-view with a high repetition rate—and without interfering with the movement—photons can also be used to control molecular shuttles. We have used, for example, the photo-detachment of a ‘caging’ group from ATP to control the availability of fuel to the motors. A similar technique, taking advantage of photo-cleavable biotin linkers, can potentially be used for the controlled unloading of cargo. Optical tweezers can be used to create well-defined forces on the order of a few pN, opposing the action of individual motor proteins and leading to insights into force creation and mechanisms of movement.

We are currently putting molecular shuttles to work as transporters in lab-on-a-chip devices, as self-propelled probes in surface imaging, and as miniature actuators for force measurements. These applications are often inspired by the many uses of motor proteins in natural organisms, providing a rapidly expanding list of novel applications that illustrate new engineering solutions made possible through biomanotechnology.

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References
First self-assembled micro-robots powered by muscle

Complex and versatile biological units, cells have extremely elaborate mechanisms to sustain, regulate, and assemble themselves. Muscle cells also have their own unique features, such as high-order organization at the molecular level, high power density, and the ability to use glucose as energy. Engineering these amazing cells onto electronic microchips is an initial, but key, step to fabricating autonomous intelligent hybrid micro-machines that can be directly powered by glucose via physiological fluids and can respond to environmental stimuli.

We have recently made significant progress in this work. A novel self-assembly system for automatically integrating cardiac muscle cells from neonatal rats on a silicon-based mechanical skeleton has been established. Using this system, we have fabricated a group of muscle-powered micro-robots. Engineering muscles to fabricate artificial robots, such as swimming fish, had already been done using conventional techniques. However, we employed self-assembly, eliminating the need for a muscle-bundle isolation step and subsequent manual integration of the isolated tissues with the mechanical structure. More importantly, in the context of our work, self-assembly means that the individual cells can not only localize where desired, but also automatically self-assemble onto the legs as described below.

To spatially-self-assemble individual cells onto functional muscle tissues, a polymer called poly-N-isopropylacrylamide (PNI), which can undergo phase transitions in water in response to environmental temperatures, was introduced. It was incorporated onto the microfabricated machine components through patterning. This intelligent polymer has the ability to fill the gap between terminals and support cells for their healthy growth and differentiation during the assembly period. The PNI subsequently dissolves in the culture medium to release the assembled tissues, thus enabling their freedom to contract at room temperature. In addition to being a sacrificial material, this polymer is also a negative material that inhibits cell growth. Were this not the case, the individual muscle cells would grow erratically and form a tissue layer, rather than oriented bundles.

Gold film has been shown experimentally to be a positive material, thus it has the ability to promote cell growth. The element also has excellent tensile strength, oxidation resistance, and can be tailored easily. The combined integration of PNI and Au with Si-based microdevices has, therefore, allowed us to fabricate the first self-assembled muscle-powered micro-robots: they have a maximum moving speed of about 40 µm/s and can work for more than four hours, though not continuously.

The Au-film thickness has dramatic effects on the motion observed from the assembled muscle bundles: a thicker film leads to a bending motion, while a thinner film results in a contraction. The bending motion reduces friction, enabling the robots to quickly move forward. In addition, the metal film store the energy from the muscles’ contraction, the release of which allows the legs to relax. In analysis of the detailed moving mechanism of the micro-robots (see Figure 1), it was found that friction played a crucial role in robot motility.

We also worked with material interfaces and phase-transition issues. In order to control the tight adhesion of cells at desired locations, at least three types of interfaces had to be dealt with: living/non-living components, mainly muscle/Au, organic/inorganic materials such as PNI/Si and Au/Cr/PNI; and inorganic/inorganic materials such as Au/Cr/Si. In addition, two-material phase-transition processes were considered in order to guarantee the freedom of motion of the muscles and their integrated devices when needed. First, the PNI liquid solution dries to a solid (for the subsequent deposition of the Au films), then it transitions from a solid gel state to a liquid solution, after which it finally dissolves in the culture medium to release the muscle bundles and devices.

Subsequent work will include the integration of our system with piezoelectric materials which, on exposure to the motion-induced stress, undergo a deformation that causes them to generate electrical charge. Our idea is to integrate a muscle bundle with a piezoelectric unimorph, with the force produced by the muscle used to deform the piezoelectric component. Such muscle-powered generators are under development and, if successfully realized, will demonstrate that glucose—a ubiquitous renewable source—can be converted to electrical energy. Eventually, such devices might be used to power MEMS devices or stimulate damaged nerves.

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Figure 1. Schematic diagrams show the sequential movement of the second microrobot during one step. (A) Before contraction of the leg. (B) During contraction of the leg. (C) After relaxation of the leg. Blue, green and red bars mark the start positions of the inorganic scaffold and the motile leg, and the final position of the motile leg, respectively.
Myosin motors show their muscles in nanotechnology

We are working to use molecular motors for the controlled transportation of cargo for nanotechnological applications, mimicking transportation processes in the living cell. Myosin is the molecular motor underlying muscle contraction and several other cellular processes: myosin molecules are organized into well-ordered filaments from which myosin motor domains extend and bind to filaments of another protein called actin (Figure 1a). There is overwhelming evidence that muscle contraction occurs as a result of structural changes in the myosin motor domain, powered by the cellular fuel, ATP (adenosine triphosphate). On the basis of these structural changes the motor domains, like a tug-of-war team, translocate the rope-like actin filaments producing shortening of the muscle.

The in vitro motility assay has been an immensely valuable technique for studying the actin-myosin function. Myosin molecules and actin filaments are first isolated from minced muscle by biochemical purification methods. Myosin molecules are then allowed to bind to a surface in a disordered arrangement (Figure 1b). Subsequently, fluorescence-labeled actin filaments may be observed as they are propelled by the myosin motors fuelled by ATP. A key limitation of this assay is that the motor proteins are disordered on the surface. Thus, methods that can position and orient them would be a major improvement, allowing basic studies of motor-protein function in an ordered arrangement similar to that in the living cell. Furthermore it would open for the use of molecular motors in controlled cargo transportation.

We and others have therefore started work to reconstitute motor protein order in vitro using micro- and nanofabrication techniques to create a motor-protein chip. Here we focus on our recent experiments with the actin-myosin system. Since the actin filaments are rather flexible, rectification of their sliding requires a track width significantly less than 1nm. To achieve this, we have used state-of-the-art nanopatterning methods such as electron beam and nanoinprint lithography to create tracks for myosin-motor immobilisation and subsequent guidance and rectification of actin-filament sliding. Most often we have used a bilayer resist system (see Figure 2) for the creation of protein tracks and the suppression of myosin function outside tracks, respectively. This system has now been markedly improved. Thus, by fine-tuning the composition of the ATP-containing solution, and by exchanging the protein-binding resist for chemical-vapor-deposited trimethylchlorosilane monolayers, we have achieved complete confinement of function with no ‘untamed’ filaments moving outside the allowed tracks.

Furthermore, the use of high-throughput nanoinprint lithography will enable us to develop the motor-protein chip into a routine biological-testing system with important future implications for drug testing and so forth. A disposable chip would also facilitate the use of motor proteins as nanomechanical components in commercial devices. The feasibility of such applications is supported by our recent observation that myosin function may be preserved for up to 12 days on trimethylchlorosilane-derivatized surfaces.

In a factory-on-a-chip application, the task of the motor proteins would be to transport molecular cargoes—e.g. enzymes—between different chip locations. It would be particularly interesting to achieve modes of transport, e.g. in closed loops, that are not readily achieved using microfluidics. As a prerequisite for the development of a factory-on-a-chip, we recently demonstrated the cargo-carrying capability of myosin-propelled actin filaments.

Thus, streptavidin-labeled CdSe quantum dots were readily attached to, and transported by, biotin-labeled actin filaments: achieved without limiting the maximum sliding velocity. Considering the quantum dot diameter (>10nm), this result suggests that most enzymes (<10nm) would be readily transported by actin filaments.

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Figure 1. The actin-myosin motor system. A: Schematic illustration of ordered arrangement of the myosin II molecules and actin in living cells with indication of different parts of myosin molecule. Crystallographic structure of myosin head (upper right) printed using The Protein Explorer software. Except for the crystal structure, the drawing is approximately to scale with an actin-filament diameter of 5-10nm.
B: Schematic illustration of a conventional in-vitro motility assay. Isolated myosin molecules in a disordered arrangement on the surface cause the actin filaments to slide in random directions in the presence of ATP (indicated by curved arrow).
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Figure 2. Nanosized tracks for myosin binding and actin-filament sliding. A and B: AFM topography images showing nanostructured surface (created by electron beam lithography) with protein-binding tracks of polymer resist MRL-6000 on floor of the grooves (350nm deep) opened up in PMMA. C: Sum of three fluorescence-microscopy images (at 6s intervals; 0.2s exposure time) of an actin filament moving to the right along a nanosized track (weakly fluorescent line).