

Using Nanoconfinement to Tailor Semiconducting Polymers:  
New Generation Optoelectronics

B. G. Sumpter<sup>1</sup>, P. Kumar<sup>2</sup>, A. Mehta<sup>3</sup>, M. D. Barnes<sup>3</sup>, W. A. Shelton<sup>1</sup>, R.  
J. Harrison<sup>1</sup>

<sup>1</sup> Computer Science and Mathematics Division

<sup>2</sup> Department of Chemistry, University of Tennessee

<sup>3</sup> Chemical Sciences Division

Oak Ridge National Laboratory

Oak Ridge, TN 37831

## Summary and Conclusions

Semiconductors and other inorganic crystals are the basis for electronics and other technologies, but aside from small changes available by doping with impurities, their chemical properties are fairly inflexible. Soft materials such as polymers, on the other hand, have almost unlimited possibilities since the chemical repeat groups can be modified to suit a particular application. However, commonly used techniques capable of producing the needed types soft-materials structures such as thin-film or self-assembly processes suffer from substrate and other molecular interactions which may dominate or obscure the underlying polymer physics. In order to minimize these complexities we have recently explored ink-jet printing methods for producing polymer particles with arbitrary size and composition. This method is based on using droplet-on-demand generation to create a small drop consisting of a very dilute polymer mixture in a solvent.<sup>1,2</sup> As the solvent evaporates, a polymer particle is produced whose size is defined by the initial size of the droplet (typically between 5 and 30  $\mu\text{m}$ ), and the weight fraction of polymer (or other non-volatile species) in solution. Because the droplets are produced with small

excess charge during ejection from the nozzle, this approach lends itself naturally to spatial manipulation of micro- and nanoparticles using electrodynamic focusing techniques.<sup>3</sup> The polymeric particles in the micro- and nanometer size range provide many unique properties due to size reduction to the point where critical length scales of physical phenomena become comparable to or larger than the size of the structure. Applications of these types of particles take advantage of high surface area and confinement effects, leading to interesting nano-structures with different properties that cannot be produced using

By combining experimental observations and developments with extensive computational chemistry studies we have substantial evidence indicating highly ordered rod-shaped structures for single molecule MEH-PPV and CN-PPV systems. The chain organization is crucial to the photophysical properties and can be controlled to a large extent by the solvent. A relatively bad solvent leads to a structure that is tightly folded into a rod-shaped morphology while a good solvent produces structures with little or random folding and more of a defect, extended-chain morphology. Secondary structural regularity is also induced by producing single molecule nanoparticles from micro-droplets of the solution without the presence of a substrate. For toluene and THF solvent preparations of MEH-PPV and CN-PPV, the resulting solvent-free single molecule nanoparticle structures show a very high level of organization consisting of  $\pi$ -stacked folded chains. Due to this structural organization which imposes a rod-shaped morphology, single molecule nanoparticle orientation on an appropriate surface occurs such that the particle stands on its end with near-perfect z-orientation. This orientational alignment is caused by excess charges that are induced on the particle during its production which tend to localize at the surface causing the rod-shaped particle to minimize the Coulombic interactions with the surface (Si-O)<sup>-</sup> groups. The excess charge also appears to increase the structural organization into  $\pi$ -stacks. The resulting z-oriented single molecule rod-shaped nanoparticles are organized into something

like a core-shell system, where the inner core is a self-solvated PPV system with inter-chain distances  $\sim 0.3$  Å closer than the surrounding chains. Since there is still orbital overlap throughout the system, facile fluorescence resonant energy transfer without the emission of a photon can occur to the core emission site. In addition this type of inter-chain distance anisotropy can give rise to behavior observed for a single quantum emitter in a dielectric medium at the nanometer scale (Rayleigh scattering regime) and thus show strong effects due to classical electromagnetic interactions (vacuum fluctuations are altered from boundary reflections) which would lead to the observed altered fluorescence lifetimes.

**The overall ramifications of developing this fundamentally new processing technique for generating optoelectronic materials, is far-reaching. By achieving uniform orientation perpendicular to the substrate with enhanced luminescence lifetimes and photostability under ambient conditions, the door is now open for major developments in molecular photonics, display technology and bio-imaging, as well as new possibilities for optical coupling to molecular nanostructures and for novel nanoscale optoelectronics devices.**

---

<sup>1</sup> C-Y. Kung, M. D. Barnes, N. Lerner, W. B. Whitten, and J. M. Ramsey, *Applied Optics* **38**, 1481 (1999).

<sup>2</sup> M. D. Barnes, K. C. Ng, K. Fukui, B. G. Sumpter, and D. W. Noid *Macromolecules* **32**, 7183 (1999).

<sup>3</sup> K. C. Ng, J. V. Ford, S. C. Jacobson, J. M. Ramsey, and M. D. Barnes, *Review of Scientific Instruments*, **71**, 2497 (2000).