Molecular association of [6,6]-phenyl-C61-butyric acid methyl esters (PCBM) with conjugated polymers relevant to organic photovoltaic cells

S.M. Mortuza and Souvik Banerjee
School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164

Introduction
Thin-film Organic Photovoltaics
- Flexible, cheap, low weight, easily manufactured.
- Bulk heterojunction, photoactive layer comprising:
  - Organic polymer (poly(3-hexylthiophene) (P3HT)).
- Power conversion efficiency ~10%.
- Varying relative concentration of PCBM and P3HT may provide a way to create suitable networks for transporting holes to photoanode and electrons to photocathode respectively.

Objectives
- To investigate the mechanisms that govern molecular rearrangement, agglomeration and transport of PCBM and P3HT.
- To correlate the morphology of the photoactive layer with key synthesis parameters such as relative concentration of PCBM and P3HT, temperature, PCBM-solvent interactions and PCBM-P3HT interactions.
- To determine the best choice of solvents and optimum relative concentration of polymer and nanoparticle for improved morphology of the photoactive layer.

Computational Model
- Gromacs 4.5.5 molecular dynamics (MD) simulation package was used.
- OPLS-AA force field with Girifalco’s Lennard-Jones (LJ) parameters associated with fullerene were taken.
- Equilibrium run was performed for at least 1 ns.
- NPT production run was conducted for at least 70 ns.
- Stochastic velocity rescaling thermostat and Parrinello-Rahman isotropic barostat was employed.
- Electrostatic interactions were computed using the Particle-Mesh Ewald (PME) method with a cutoff distance of 1.5 nm.
- Cluster size of PCBM was calculated based on the distance between centers of mass (COM) of fullerenes.
- Potential of mean force (PMF) of fullerenes were evaluated in different solvents using the umbrella sampling method.
- Systems with PCBM and solvents were simulated at 280 K, 290 K, 300 K, 310 K and 320 K.

System's PCBM : solvent weight ratio PCBM Solvents
P1T1 1:1 50% Toluene
P1T2 1:2 33% Toluene
P1I1 1:1 50% Indane
P1I2 1:2 33% Indane
P1T11 1:1 50% Toluene + Indane
P1T22 1:2 33% Toluene + Indane

P, T and I designate PCBM, toluene and indane respectively.

Results

PCBM with solvents
- Cluster sizes of PCBM increase with the increase of concentration of PCBM and processing temperature.
- Cluster sizes of PCBM are larger in toluene than indane and toluene-indane mixture.
- Larger PCBM clusters are dominant in systems comprising toluene.
- Number of fullerenes that surround a single fullerene at 1.2 nm is more in toluene than indane and toluene-indane mixture.
- The PMF plot indicates that the binding energy between fullerene is greater in toluene than in indane.
- Aromatic phenyl rings of PCBM help to increase the solubility of PCBM in the solvents.
- The ester chains of PCBM associate with each other in the clusters.
- Toluene relaxes quicker than indane and relaxation time of solvent molecules decrease with the decrease of concentration of PCBM.

PCBM with P3HT
- Increased contact surface area between PCBM and P3HT is obtained, since PCBM are surrounded by P3HT molecules.
- At relatively high concentrations, PCBM form clusters due to interaction between the fullerene moieties.
- In the system with 1:1 PCBM-P3HT, PCBM and P3HTs form separate networks that transport holes to photoanode and electrons to photocathode respectively.

Conclusions
- PCBM form large clusters in toluene while they are relatively dispersed in indane, which indicates the greater solubility of PCBM in indane than in toluene.
- PCBM cluster sizes increase with the increase of PCBM concentration and processing temperature.
- In toluene-indane mixtures, PCBM are clustered to a greater extent than in indane and less than that in toluene.
- The binding energies between fullerenes are 0.85 kcal/mol in toluene and 0.40 kcal/mol in indane indicating relatively enhanced hydrophilic behavior of PCBM in indane compared to that in toluene.
- Toluene-indane mixture can provide a way to tune desired agglomerate size distribution of PCBM and P3HT in the photoactive layer to achieve greater efficiencies.
- Varying relative concentration of PCBM and P3HT may provide a way to create suitable networks for transporting holes to photoanode and electrons to photocathode respectively.

Future Work
- Our next goal is to understand the molecular mechanisms that govern the formation of PCBM and P3HT agglomerates in the photoactive layer.
- Obtain structure factor from coordination numbers and compare them with experimental results.
- Evaluate diffusion coefficients of P3HT and PCBM in the solution.
- Investigate a wide range of nanoparticle-polymer systems to identify the most promising combination for use in OPV solar cells.

References

Acknowledgement
The authors gratefully acknowledge support from 3M Foundation and fruitful discussions with Dr. Nikos Kopidakis at the National Renewable Energy Laboratory (NREL).

Contact Information
Please contact: s.mortuza@wsu.edu or souvik.banerjee@wsu.edu for further information.