Self Assembly – From Molecules to Photoluminescent Cables

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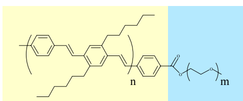
Motivation

There is a significant knowledge base concerning the design of molecular species with desired functionalities such as conductivity, magnetism, and optics. However, interesting molecular properties may not translate into interesting solid-state physical properties, unless one is able to control the structural packing at the same time. Our diblock copolymer approach allows us to control the packing morphology while retaining the built-in functionality.

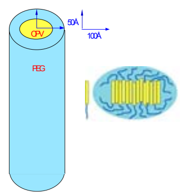
Background



OPV_n-PEG_m

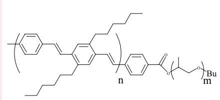
- OPV, oligo(phylenevinylene), block is rigid, hydrophobic, and photoluminescent.
- PEG, poly(ethyleneglycol), block is flexible and hydrophilic.
- OPV-PEG macromolecules self assemble in solution to form nanofibers.

- Based on small angle neutron scattering (SANS) results, these nanofibers have radii around 8 nm.
- The cross section consists of OPV inner core and PEG outer shell with monolayer packing motif.
- The radius of the inner core is ~5.2 nm.
- The length of the PEG segment indirectly controls the overall length of the nanofibers.



Major Accomplishment

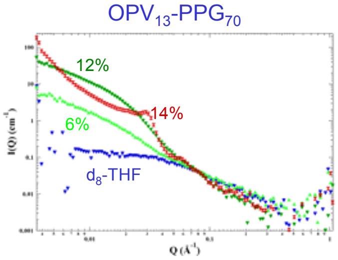
- By replacing PEG with PPG, poly(propyleneglycol), we can control the entire self assembly process from individual molecules to multi-fiber cables.
- With the core-shell structure, excitation on one segment of the fiber bundle illuminates the entire fiber bundle.



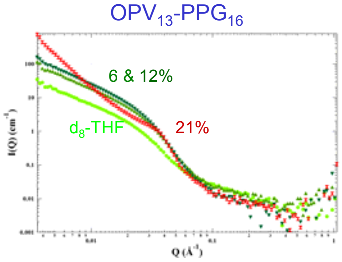
OPV_n-PPG_m

Results

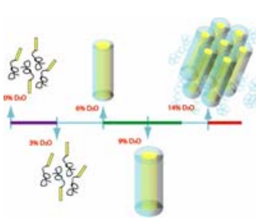
OPV_{13}-PPG_{70}

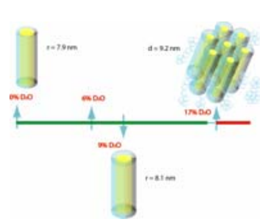


OPV_{13}-PPG_{16}



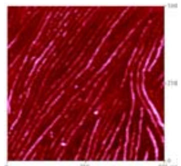
- For OPV-PPG_{70}, no aggregation below 6% water, random nanofibers between 6 and 12% water, and ordered fiber bundles above 14% water.
- For OPV-PPG_{16}, nanofibers were observed without water and partially ordered fiber bundles above 17% water.





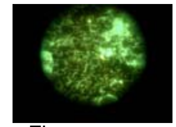
OPV_{13}-PPG_{70}

Fluorescence micrograph

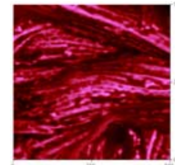


AFM image 500×500 nm

OPV_{13}-PPG_{16}



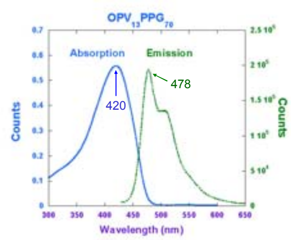
Fluorescence micrograph



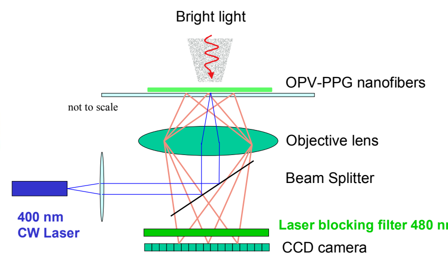
AFM image 500×500 nm

- AFM images taken from one of the fiber bundles visible in the fluorescence micrographs reveal partially aligned individual nanofibers.
- OPV-PPG_{70} forms nanofibers a few micrometer long and 18 nm in diameter.
- OPV-PPG_{16} forms short nanofibers with comparable diameter.

Will light travel along these nanofibers?

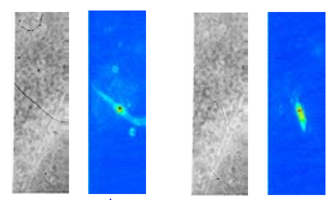


Absorption and emission spectra of OPV_{13}-PPG_{70} in THF

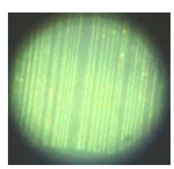


Schematic diagram of microspectrometer for local excitation of a single nanofiber bundle

- Gray scale bright light images of two OPV_{13}-PPG_{70} fiber bundles (Image size: 32×102 μm)
- Each fiber bundle was locally excited at 400 nm and detected at 480 nm showing fluorescence from the entire fiber bundle.

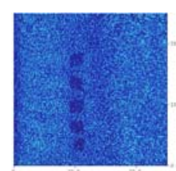


Fluorescence images



Fluorescence image of a micrometer size bar code pattern

With hydrophobic cores and hydrophilic shells, these nanofibers can easily be attached to patterned areas for sensor applications.



2×2 μm² squares of OPV-PEG developed with dip-pen technique

Impact

- Control of the self assembly processes and the sizes of the nanofibers have been demonstrated.
- These nanofibers may be used for sensor, wave guide, or lasing devices.

Future Direction

- Infiltration of nanofibers into Si trenches for fiber alignment and photonic applications
- Testing for wave guide and lasing properties

Syntheses of Amphiphilic Diblock Copolymers Containing a Conjugated Block and Their Self-Assembling Properties, H. B. Wang, H. H. Wang, V. S. Urban, K. C. Littrell, P. Thiyagarajan, L. Yu, J. Am. Chem. Soc. 122, 6855-6861 (2000)

BES - DOE

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