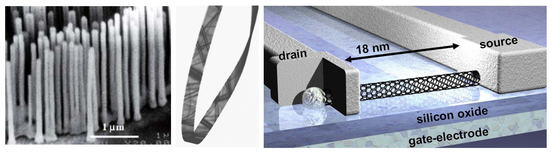
Organic Nanowires and Nanobelts

Fabrication through Self-Assembly, 1D Confined Optical and Electrical Properties

USTAR — Turning innovation into industry.

Why one-dimensional (1D)?

→ Miniaturization of devices;
→ Higher sensitivity and selectivity;
→ New, novel phenomena and concepts in materials design.



1D **inorganic** nanowires, nanotubes, nanobelts, (whatever named), have been extensively studied for both metals and semiconductors.

1D organic much less studied.

Advantages of Organic Materials:

- **Unlimited choices of molecules:** electronic structure (color), configuration, size, shape …
- **Easy to modify:** chemical interactions.
- **Flexible for processing:** vapor, liquid/solution, solid.
- **Adaptable** to various substrate.
- **Cheap** for manufacturing, processing, packaging.
- Strong, tunable **fluorescence** emission: optical sensing.

Accounts of Chemical Research, 41 (2008) 1596-1608.

It still remains a challenge how to assemble molecules into **1D** nanostructures, as it requires a tight interplay between molecular design and synthesis (chemistry) and the materials fabrication and characterization.

Combined approach to 1D self-assembly

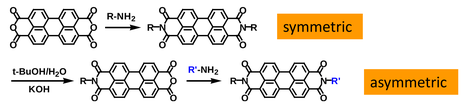
Thermodynamic Optimization through Molecular Design and Synthesis: *to optimize the co-facial π–π stacking, leading to 1D assembly.*

Combined

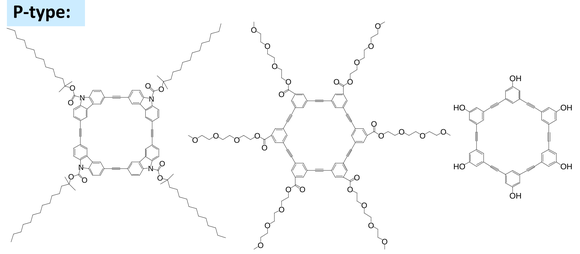
Kinetic control through Solution Processing: *to max. the 1D growth of the assembly.*

Complementary building-block molecules

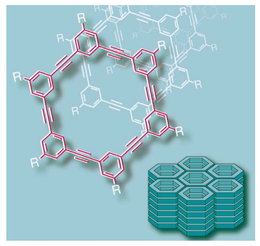
N-type:



P-type:



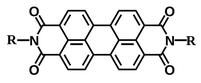
A unique p-type semiconductor *(electron donor)*



Arylene Ethynylene Macrocycle (**AEM**)

- Large, rigid, planar surface favors π–π stacking;
- Tunable sizes for tubular structures;
- Flexible structure and property modification: redox, binding, etc.

A unique n-type semiconductor *(electron acceptor)*

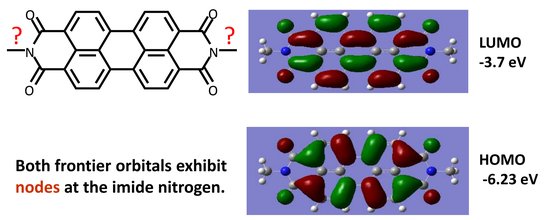


Perylene tetracarboxylic diimide (PTCDI)

- High fluorescence yields.
- High thermal, chemical and photochemical stability.
- Strong tendency to aggregate via π-π stacking between the perylene units.
- ***n-type*** semiconductor characteristics as compared to more common **p-type**.

Broad applications in ***thin-film*** optoelectronic devices: LCD's, LED's, FET's, solar cells, and chemosensors, etc.

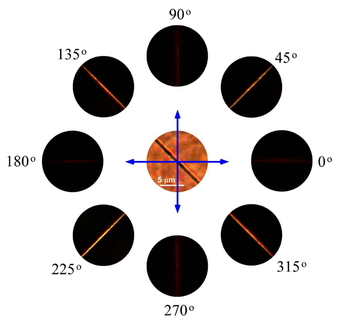
Flexible structural modification



Both frontier orbitals exhibit nodes at the imide nitrogen.

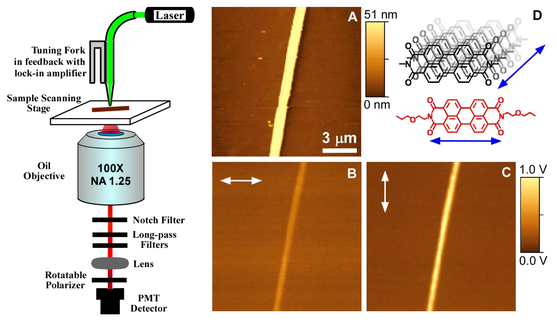
Modification of side-chain structures leads to no alteration of the electronic property of PTCDI, but affect the conformation and strength of molecular π–π stacking.

1D optical property: *Cross-Polarized*



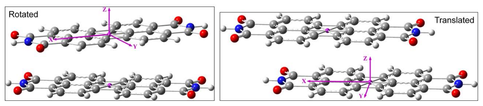
J. Am. Chem. Soc. **127**(2005) 10496-10497

Linearly polarized emission : *single-nanobelt by NSOM*



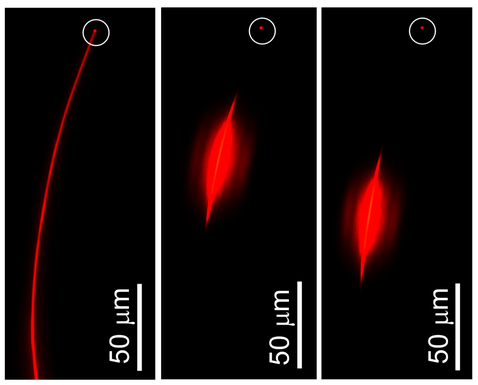
J. Phys. Chem. B, **110** (2006), 12327-12332

Transition dipole moment depends on stacking conformation

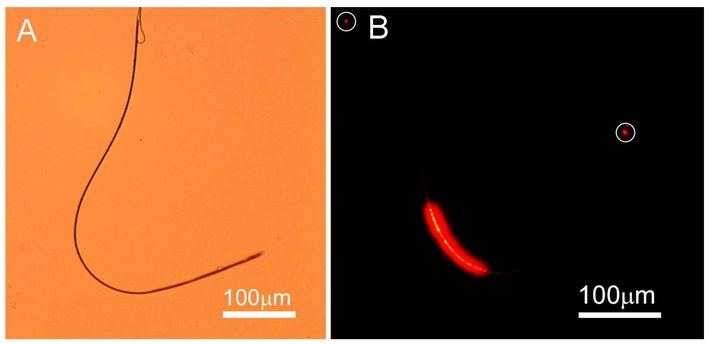


Stacking distance: 3.4Å, Rotated: 30°				Stacking distance: 3.4Å, X-slide: 2.67Å, Y-slide: 0.36Å			
Transition dipole moment along X-Y-Z (ground to the lowest excited state):				Transition dipole moment along X-Y-Z (ground to the lowest excited state):			
X	Y	Z	Oscillation strength	X	Y	Z	Oscillation strength
0.0762	0.2847	0.0000	0.0041	2.1411	0.0518	0.4317	0.2174

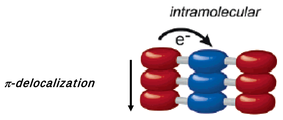
Waveguide: *1D confined optics*



Waveguide: *no bending loss*

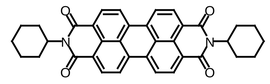


- Enhanced charge mobility due to π–electron delocalization.
- Increased exciton migration π–π interaction (energy hopping).
- Increased lateral (or intramolecular) charge separation due to enhanced vertical charge mobility.

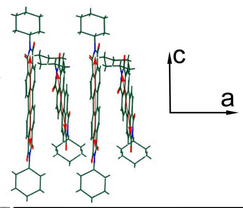


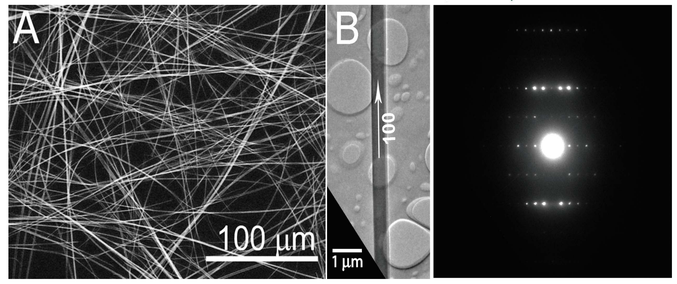
Exciton diffusion, Charge separation, Charge transport --- three major factor affecting efficiency of organic optoelectronic devices, like solar cells.

A nanobelt composed of rotated stack

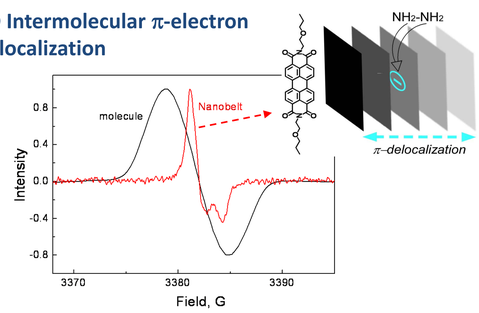


Chem. Mater. 21 (2009) 2930–2934.



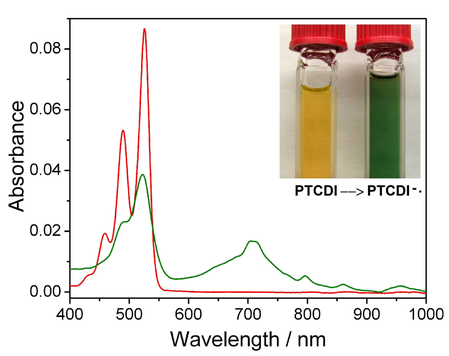


1D Intermolecular π-electron delocalization



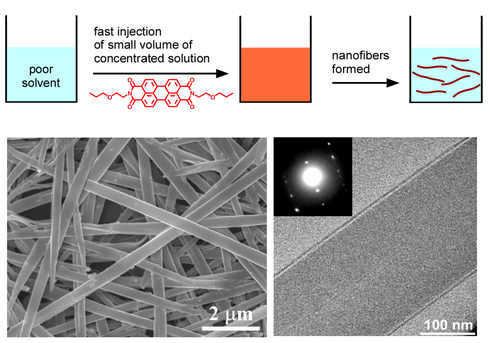
- ESR spectrum of nanobelt loses the reflection symmetry about the line center;
- Anisotropic g-tensor, with g⊥ (2.0038) > g// (2.0026), is implicative of the *intermolecular* π–delocalization along the long axis of molecular stacking.

High stability of PTCDI anionic radical due to intramolecular π-delocalization

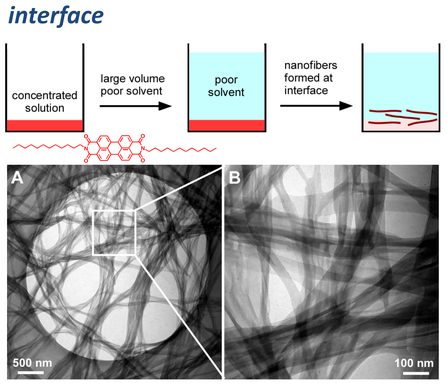


J. Am. Chem. Soc. **129** (2007) 6354-6355

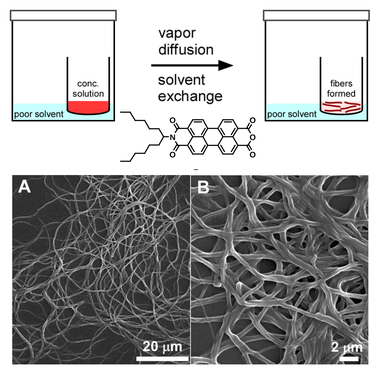
Fast injection: *bulk phase self-assembly*



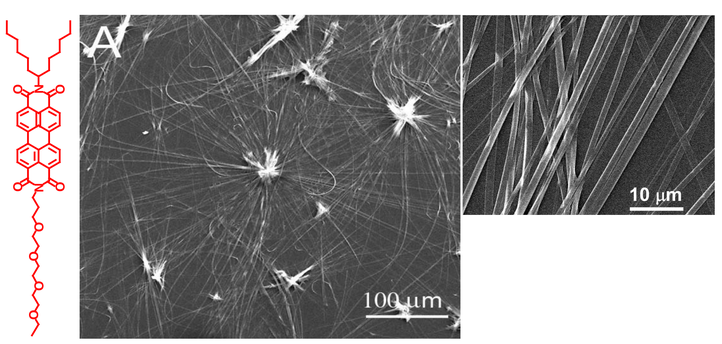
Binary phase transfer: *self-assembly at interface*



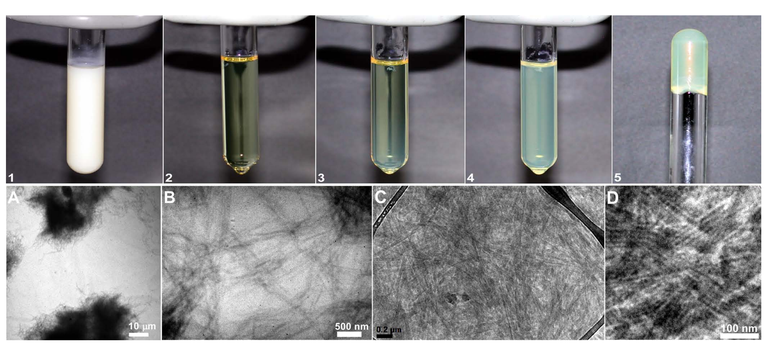
Vapor diffusion: *slow phase transfer*



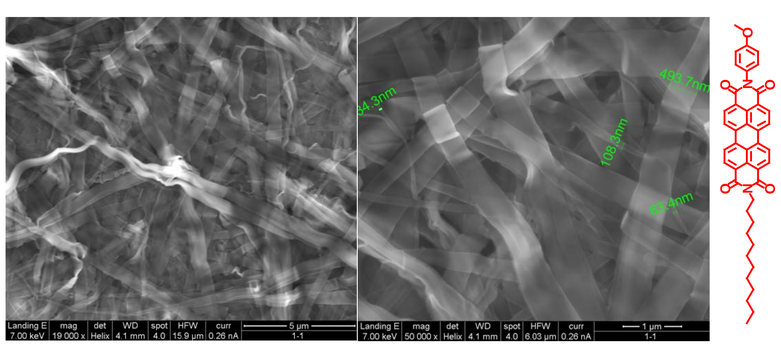
Seeded growth: *ultralong nanobelts*



Sol-gel: *control through temperature*



Ultrathin nanoribbons for enhanced optoelectronic performance



THE UNIVERSITY OF UTAH

The Zang Research Group, Department of Materials Science and Engineering
Tel. 801-587-1551, Email: LZang@eng.utah.edu, Web: www.eng.utah.edu/~lzang