Bioinspired Materials: Basic Physics and Applications

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Nanostructured Materials

Inorganic World

Biological World

Bioinspired Materials

Elastic Fibrils

Peptide Nanotubes
Vapor Deposition Technology
Biological and Bioinspired Materials at Nanoscale

Living Nature: Protein Fibers

Natural Nanofibrils

- Human Bone Collagen

Amyloid fibrils

- Alzheimer amyloid nanofibrils
Nature: Amyloid Fibrils

There are ~ 20 distinct human diseases that are associated with amyloid fibrils formation: regular fibrillar structures micrometers in length, a few nanometers in diameter

Amyloid Fibrils—NATURAL BIOLOGICAL NANOFIBRILS

The transition from the native state conformation to amyloid fibrils

Soluble Peptides and Proteins

Insoluble Amyloid Fibrils

Alzheimer filaments diam.
10-15 nm, few mm length

Alzheimer’s β-amyloid peptide


TTR amyloid fibrils
in cerebrospinal fluid

M. Hayden, S. Tyagi, 2001

Endocrine pancreas,
amyloid fibrils

T. Kowalewski, D. Holtzman,
PNAS, 1996

β2-microglobulin amyloid fibrils

S. Takahashi, Osaka Univ, 2006
Bioinspired Peptide Nanotubes

Peptide Engineering:
D- and L-amino-acid cyclic peptide

Bioinspired Chemically Synthesized Molecules - Core Motif of Alzheimer disease

FF peptide

SEM image

Aqueous solution


New Generation of Bioinspired Materials
Bioinspired Peptide Nanotubes

Peptide Engineering:
D- and L-amino-acid cyclic peptide

Bioinspired Chemically Synthesized Molecules - Core Motif of Alzheimer disease


The Question is:
What Do We Know About These New Nanostructures?

– Peptide Engineering

New Generation of Bioinspired Materials
Biological and Bioinspired Structures

Nanocrystalline Building Blocks Linked by Noncovalent, Weak Interactions

Self assembly mechanism
R. Ghadiri, Angew. Chem. 2001

M. Perutz, Adenovirus-based on peptide fibrils, J Biol. Chem, 2005

Makin, O. S., Amyloid Fibrils (Alzheimer) Febs J. 2005


2D Supramolecular Structure of Carboxylic Acids
P. Samori, Adv Mater, 2010

D- and L-amino-acid cyclic peptide

Electron diffraction
Common Basic Features:
1. Identical core biomolecule composition
2. Similar molecular recognition and self assembly mechanisms
3. Supramolecular nanofibrillar structures containing nanoscale crystalline elementary building blocks assembled due to noncovalent weak, reversible, dynamic interactions

Common Intrinsic Physical Properties?
Biological and Bioinspired Structures: Motivation and Goals

1. Basic Intrinsic Properties at the Interchange Physics-Biology
2. Self Assembly Mechanism
3. New Generation of Nanostructural Bioinspired Materials

- Nanophotonics (Bio-LEDs, Bio-Lasers, Non-Linear Optical Converters, etc)
- Nanopiezotronics, Nano-Bio-Piezotronics and Bio-Piezoceramics
- Energy Storage Devices (Batteries and Supercapacitors)

Could Self Assembly Bioinspired Peptide Nanostructures be a Model of Biological Materials?
Part I

Bottom-up Nanotechnology of Bioinspired Peptide Nanostructures

Self Assembly - Technology Developed by Nature

E. Gazit, Science, 2003

Evaporated from Solution Peptide Nanotubes

Rosenman, Gazit, Nature Nanotechnol, 2009

Vapor Deposited Peptide Nanotubes
Peptide Engineering and Self Assembly Mechanism

M. R. Ghadiri, Nature, 1993,

D- and L-amino-acids (8 units forming Cyclic Peptide)

Striations in the TEM image are ~ 18 Å
diameter of peptide ring
Subunit distances of 4.8 Å

Elementary Building Block
2 Peptide Molecules
Peptide Nanotubes Vapor Deposition
Nature Nanotechnology, 2009
Peptide Nanotubes Vapor Deposition
Nature Nanotechnology, 2009


Regular Cross Section: Tetragonal Symmetry $\mathbb{I}_4$
Substrate

Peptide Nanotubes Vapor Deposition
Nature Nanotechnology, 2009


Regular Cross Section: Tetragonal Symmetry $I_4$

Self Assembly Mechanism?
Elementary Building Blocks?
Peptide Nanostructures

Recent Publications

- ACS Nano (2010)
- Advanced Materials (2010)
- J. of Materials Research (2010)
- Ferroelectrics (2010)
- JACS (2010)
- J. Pept Sci (2011)
- J. Biomacromol (2011)
Part II

Optical Properties of Bioinspired Materials: Nanostructure and Quantum Confinement


Could This Nanotube Be A Quantum Well Structure?
Self Assembled Bio-Inspired Peptide Nanotubes

**FF-Peptide Monomer**

![Chemical Structure of FF-Peptide Monomer](image)

**The Same Monomer Diphenilalanine FF-Peptide**

- **FF-peptide nanofibers** (vapor deposition)
- **FF-peptide nanotubes** assembled in liquid

**Monomer Diphenilalanine, Aqueous Solution**

- \(\lambda(\text{PL}) \approx 285\text{nm}, \Delta \lambda \approx 30\text{ nm}\)
- \(\lambda(\text{Abs}) \approx 257\text{nm}\)

![Absorption and Photoluminescence Spectrum](image)

Optical Absorption of Self Assembled Bio-Inspired Peptide Nanotubes

FF-peptide nanofibers (vapor deposition)

Nature Nanotechnol, 2009
Nano Letters, 2009

FF-PNT, assembled in liquid

10 μm

Optical Absorption

Step-like absorption

Peak-like Optical Absorption

JACS, 2010
Quantum Confinement Phenomena

L \sim \lambda \text{(de Broglie wavelength of an electron, } \lambda \sim 10\text{-}40 \text{ Angstrom)}

Optical Absorption is Defined by Electron Density of States

\Delta E \sim 10^{-15} \text{ eV}

\epsilon_n^2 - 2m(L)
Quantum Confinement Phenomena

$L \sim \lambda$ (de Broglie wavelength of an electron, $\lambda \sim 10-40$ Angstrom)

Bulk crystal

3D

Quantum well

2D

Quantum dot

1D

$L(Z) \sim \lambda$

Density of States

$\Delta E \sim 10^{-15}$ eV

$N(E) = \frac{m^*}{\pi \hbar^2}$

$E_n = \frac{\hbar^2}{2mL}$
Quantum Confinement Phenomena

L~λ (de Broglie wavelength of an electron, λ~10-40 Angstrom)

Bulk crystal

Quantum well

Quantum dot

ΔE~10^{-15} eV

DENSITY OF STATES

ENERGY

N(E) = \frac{m^*}{\pi \hbar^2}

ΔE~3-4 eV

ΔE~1 eV

ΔE

E_n = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2
Quantum Confinement Phenomena

L~\lambda (de Broglie wavelength of an electron, \lambda\sim10-40 \text{ Angstrom})

Bulk crystal

\[ L(X,Y,Z)\sim 1 \text{ cm} \]

Quantum well

\[ L(X,Y)\sim 1 \text{ cm} \]

Quantum dot

\[ L(Y)\sim \lambda \]

\[ L(Z)\sim \lambda \]

Density of States

\[ \Delta E\sim 10^{-15} \text{ eV} \]

Optical Data-Virtual Probe Microscopy

\[ E_n = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2 \]
Quantum Confinement in Self Assembled Bio-Inspired Peptide Nanotubes

Monomer Diphenilalanine, aqueous solution

Absorption

Photoluminescence

\( \lambda_{(PL)} \sim 285 \text{ nm}, \Delta \lambda \sim 30 \text{ nm} \)

Absorption

\( \lambda_{(Abs)} \sim 257 \text{ nm} \)

Step-like optical absorption

2D-Quantum Confinement

PNT-Assembled from Solution

Peak-like optical absorption

OD-confinement

FF-peptide nanotubes (evaporation from solutions)

PNT, assembled

PQD, dissembled

JACS, 2010
Quantum Confinement in Self Assembled Bio-Inspired Peptide Nanotubes

Monomer Diphenilalanine, aqueous solution

Photoluminescence
\( \lambda (PL) \sim 285 \text{ nm}, \Delta \lambda \sim 30 \text{ nm} \)

Absorption
\( \lambda (\text{Abs}) \sim 257 \text{ nm} \)

FF- Vapor Deposited Peptide Nanofibers

Step-like optical absorption

2D-Quantum Confinement

PNT-Assembled from Solution

Peak-like optical absorption

OD-confinement

JACS, 2010
1. Step-like optical absorption spectra
2D-quantum confinement in self assembled FF-nanofibers
Highly Ordered Nanocrystallized QW Structure

2. Photoluminescence in UV and visible region of Exciton origin at Room Temperature

\[ \Delta E = 0.98 \text{ eV, } L \sim 10^{-13} \text{ Å} \]
**Cyclic Peptide Nanotubes-QW Engineering**

FF-peptide nanotubes (vapor deposition)

Self Assembly Process:
PNT of 10 μm length:
10,000 QW in dozen of seconds

QW structure in PNT is intrinsic structure for Laser-QW-Bio-Laser?

Quantum Well Structure
Δ~13 Å


**Cyclic Peptides** ➔ **Quantum Wells**
Cyclic Peptide Nanotubes-QW Engineering

FF-peptide nanotubes (vapor deposition)

Self Assembly Process:
PNT of 10 μm length:
10,000 QW in dozen of seconds

Could we TUNE the wavelength?

Quantum Well Structure
Δ~13 Å


Cyclic Peptides ➔ Quantum Wells
Quantum Dot Structure

Individual peptides

Quantum dots

Self-assembly

Peptide nanotubes

PQD, dissembled

Optical Absorption

Spectrum of QD

Wavelength, nm

240

280

320

JACS, October, 19, 2010

PNT, assembled

FF-peptide nanotubes (evaporation from solutions)

QD, Bio-Markers?

QD-Bio-Laser?

Δ~15 Å

Nature, N&V, 468, Nov 25, 2010
Quantum Dot Structure
Δ~15 Å

Could we TUNE the wavelength?

QD-Bio-Laser?

QD-Bio-Markers?

FF-peptide nanotubes (evaporation from solutions)

Optical Absorption

Spectrum of QD

PNT, assembled

PQD, dissembled

Nature, N&V, 468, Nov 25, 2010
Peptide Nanotubes Self Assembly Mechanism

Hydrogel Fmoc-FF

FF Fibrils

Sub-gel Quantum Dot Structure

Absorption, a.u

Wavelength, nm

Normalized PL Intensity (A.U)

Excitation

Stokes Shift, \( \Delta \lambda \approx 15 \text{ nm} \)

Absorption

\( \lambda \approx 307 \text{ nm} \)

Dynamics of Exciton Formation-Self Assembly Mechanism

Normalized efficiency

Wavelength, nm

Absorption

\( \Delta \lambda, \text{ nm} \)

Time (sec)

Normalized Intensity

0.05 mg/ml

0.1 mg/ml

0.2 mg/ml

0.3 mg/ml

0.4 mg/ml

0.5 mg/ml

0.8 mg/ml

1.5 mg/ml

2 mg/ml
Peptide Nanotubes Self Assembly Mechanism

Could Self Assembly Bioinspired Peptide Nanostructures be a Model of Biological Materials?
Self Assembly Insulin Amyloid Fibrils

C~0.5 mg/ml, d~1.3 nm

C>1.5 mg/ml, d~5 nm

C>6 mg/ml

Optical Absorption

PL Excitation

Δλ~4 nm
Part III

BIOLOGICAL AND BIOINSPIRED NANOSTRUCTURES:

FERROELECTRICITY AND RELATED PHENOMENA

Pasteur, 1860:
Biological systems have a common basic feature: pronounced chiral dissymmetric structures
Motivation and Goals

- Ferroelectric Properties in Bioinspired Nanostructures
- Bottom-up Technology
- Ferroelectric (Piezoelectric) Bioinspired Biocompatible Materials
Ferroelectricity in Biology
Piezoelectricity, SHG are Fundamental and INTRINSIC Property of Biological Materials.
Plants, animal and human tissues are Piezoelectrics.

Ferroelectric and related phenomenon
Piezoelectric effect in bones

Linear electroptic effect in nerve fibers
Tasaki, Jpn. J. Physiol, 1993

Second harmonic generation in pineal gland
Lang, IEEE Trans. on Dielectrics, 1996

Electrical Spontaneous Polarization
Pyroelectric properties in tendon and bones
Lang, Nature, 1966
Athenstaedt, Ann NY Acad. Sc., 1974
and in nerve tissue

Pyroelectric and piezoelectric properties in amino acids-based crystals
Lemanov, Ferroelectrics, 1998

Bacteriorhodopsin membrane protein
Dipole moment P~100 D, Kimura, 1984

Y. Feldman, et al
Piezoelectricity, SHG are Fundamental and INTRINSIC Property of Biological Materials. Plants, animal and human tissues are Piezoelectrics.

Ferroelectric and related phenomenon
- Piezoelectric effect in bones
- Linear electrooptic effect in nerve fibers
  Tasaki, Jpn. J. Physiol, 1993
- Second harmonic generation in pineal gland
  Lang, IEEE Trans. on Dielectrics, 1996
- Bacteriorhodopsin-membrane protein
  Dipole moment P~100 D, Kimura, 1984

Matthias: "We are made up of Ferroelectrics"

Pyroelectric and piezoelectric properties in amino acids-based crystals
Lemanov, Ferroelectrics, 1998
Piezoelectric Effect in Human Bones at Nanoscale

Piezoelectric Effect in Human Bones at Nanoscale


Piezoresponse image

Fibrils within parallel bundles in fascia tissues can have opposite polar axis orientation and are organized in small groups (domains) having the same polar orientation (180° domains).

A.Gruverman, Biophysical Journal, 2010

Collagen Type 1 Fibrils, Piezoresponse,
Ferroelectric and Related Properties in Bioinspired Peptide Nanotubes

C. H. Görbitz, University of Oslo: Structure and Symmetry of 160 Dipeptide Nanotubes:

Chem. Commun. 2006;
Acta Cryst. 2010;

Dipeptides:
LL-orthorhombic,
LF-monoclinic
FL-orthorhombic
FF-hexagonal

Space Group
P2₁2₁2₁
P2₁
P2₁2₁2₁
P6₁

Diphenilalanine (FF) Peptide Nanostructures
Ferroelectric and Related Properties in Bioinspired Peptide Nanotubes

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FF-hexagonal

Space Group
P2₁2₁2₁
P2₁
P2₁2₁2₁
P6₁

Diphenylalanine (FF) Peptide Nanostructures

Symmetry of FF-Peptide Nanostructures?
Ferroelectric Properties of FF-Peptide Nanotubes

PNT-Evaporated from solution

Self Assembly

Linear Diphenilalanine Peptide

Native PNT: Hexagonal Symmetry $P6_1$

PNT-Hexagonal Structure

JACS, 2010
Biomacromolecules, 2011
Peptide Nanotubes Piezoelectricity: Phase Transition

Piezo-Force Microscopy: cooperation with Dr. A. Kholkin (Portugal)

PFM-room temperature

1. Piezoelectric effect:
   \[ d_{15} \sim 100 \text{ pm/V} \]
   \[ d_{33} \sim 7 \text{ pm/V} \]

2. Spontaneous Polarization

ACS Nano, 2010

Piezo-Force Microscopy: cooperation with Prof. A. Gruverman (USA, Nebraska-Lincoln)

Piezoresponse
Peptide Nanotubes Piezoelectricity: Phase Transition

Piezo-Force Microscopy: cooperation with Dr. A. Kholkin (Portugal)

Macroscopic Piezoelectricity and Macroscopic Electrical Polarization in Supramolecular Structures

1. Piezoelectric effect:
   - $d_{15} \sim 100 \text{ pm/V}$
   - $d_{33} \sim 7 \text{ pm/V}$

Piezo-Force Microscopy: cooperation with Prof. A. Gruverman (USA, Nebraska-Lincoln)

ACS Nano, 2010
Peptide Nanotubes Piezoelectricity: Phase Transition

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   - $d_{33} \sim 7$ pm/V

Macroscopic Piezoelectricity and Macroscopic Electrical Polarization in Supramolecular Structures

Piezo-Force Microscopy: cooperation with Prof. A. Gruverman (USA, Nebraska-Lincoln)

Phase Transition in Supramolecular Structures
Phase Transition in FF-Peptide Nanotubes

Diphenilalanine (FF) Peptide Nanostructures

The Same Diphenilalanine Monomer BUT Absolutely Different Properties At All Levels:
Morphology, Symmetry, Molecular, Piezoelectric, SHG, Electronic, Optical, Wettability..and More

10 mm
Low Temperature Phase

T~150°C
2 μm
High Temperature Phase

10 mm

Biomacromolecules, 2011
Peptide Nanotubes Morphological Transition

Biomacromolecules, 2011

STEM

T~150 °C
Peptide Nanotubes Morphological Transition

Biomacromolecules, 2011

Hollow PNT

STEM

Hollow PNT

T~150 C

Nanofibers

Nanofiber
Peptide Nanotubes Morphological Transition

Biomacromolecules, 2011
Peptide Nanotubes Morphological Transition

-Huge Atomic Displacements
-Transition Via Amorphous State?

Irreversible Phase Transition

Biomacromolecules, 2011
Phase Transition: Wettability Properties

T~150 C

High Temperature Phase

Biomacromolecules, 2011
Phase Transition: Wettability Properties

Total Collapse of Nanochannels in PNT Due To Transition to PNF

High Temperature Phase

Biomacromolecules, 2011
After heating

Intensity (AU)

2

Before heating

Intensity (AU)

T~150°C

Centrosymmetric, Class D_{2h}

Asymmetric Structure, Class C_6

PNT-Hexagonal Structure

XRD Characterization

Orthorhombic, D_{2h}

Centrosymmetric

Hexagonal, C_6

Asymmetric

Structural Phase Transition,
T~150°C

Phase Transition: Symmetry C_6 to D_{2h}

Asymmetric Structure to Symmetric One

Peptide Nanotubes Structural Transformation
Peptide Nanotubes Structural Transformation

Asymmetric Structure, Class $C_6$

1. Low Temperature Phase
2. High Temperature Phase

XRD Characterization

Orthorhombic, $D_{2h}$

Centrosymmetric

Structural Phase Transition, $T \sim 150 \, ^\circC$

Phase Transition: Symmetry $C_6$ to $D_{2h}$

Asymmetric Structure to Symmetric One

Group-Subgroup Relationship Between the Symmetries of the Phases is Absent
Phase Transition: Molecular Transformation

Linear FF

$\Delta E = 157.98 \text{ kcal/mol}$

T $\sim 150^\circ C$

Cyclic FF

K. Joshi, Tetrah. Lett. 2008

J. Pept Sci, 2011

J. Biomacromol., 2011

Water Releasing

TGA
**Linear-FF**

**Cyclic-FF**

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**Phase Transition: Molecular Transformation**

**Linear-FF**

**Cyclic-FF**

$\Delta E = 157.98 \text{ kcal/mole}$

$T \sim 150^\circ C$

**K. Joshi, Tetrah. Lett. 2008**

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**Phase Transition:**

- Reconstruction of Covalent Bonds
- Irreversible Phase Transition

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**TGA**

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**J. Pept Sci, 2011**

**J. Biomacromol., 2011**
Phase Transition
In Bioinspired FF-Peptide Nanostructures

1. The transition is based on breaking of chemical bonds
2. Group-Subgroup relationship between the symmetries of the phases is absent
3. The transition is strongly first order

Reconstructive Phase Transition
APPLICATIONS
OF BIOINSPIRED MATERIALS:

a. Nanophotonics
b. Nanobiopiezotronics
c. Energy Storage Devices
d. Medical Technology
Self Assembly Process:
PNT of 10μm length:
10,000 QW in dozen of seconds
QW structure in PNT is intrinsic structure for Lasers

Nano Lett., 2009

Quantum Well Structure
Δ~13 Å

PNT of 10μm length:
10,000 QW in dozen of seconds
QW structure in PNT is intrinsic structure for Lasers

Nano Lett., 2009

Quantum Dot Structure
Δ~15 Å

Optical Absorption

Optical Absorption

JACS, October, 19, 2010

Nature, 468, Nov 25, 2010
Peptide Nanotubes-Nanoordering and Nanostructure

Self Assembly Process:
PNT of 10 μm length:
10,000 QW in dozen of seconds
QW structure in PNT is intrinsic structure for lasers.

Quantum Well Structure
Δ~13 Å

Nanotubes
Monomers

Optical Absorption

Spectrum of QW
Nature, 468, Nov 25, 2010

量子点结构

Δ~15 Å

Spectrum of QD
JACS, October, 19, 2010

Bio-LEDs

Nature, 468, Nov 25, 2010
Heat-treated PNT evaporated from organic solutions

Vapor Deposited PNT

Light Emitting Devices

PNT-LED

Toward Bio-Laser
Nanophotonics-Insulin Amyloid Fibrils

C~0.5 mg/ml, d~1.3 nm

C>6 mg/ml
Amyloid fibrils

PL Excitation

Δλ~4 nm
Could Self Assembly Bioinspired Peptide Nanostructures Be a Model of Biological Materials?
Could we speak about New Class of Ferroelectrics-Supramolecular Ferroelectrics of Biological Origin?

Asymmetric Peptide Structures *(J. Pept. Sci, 2011)*

- FF-Hexagonal
- Ala-Ala (AA), Tetragonal
- LL-Orthorhombic,

- Piezoelectric Properties
- Second Harmonic Generation
- Spontaneous Electrical Polarization
- Pyroelectric Effect?
Bio-Nano-Piezoelectrics

Could we speak about New Class of Ferroelectrics - Supramolecular Ferroelectrics of Biological Origin?

Asymmetric Peptide Structures (J. Pept. Sci, 2011)

FF-Hexagonal

Ala-Ala (AA), Tetragonal

LL-Orthorhombic,

Bio-Peptide Thin Films

Bio-Piezoceramics

- Piezoelectric Properties
- Second Harmonic Generation
- Spontaneous Electrical Polarization
- Pyroelectric Effect?
Nanotechnology of Elementary Building Blocks

JACS, 2010

Quantum Dot Structure
Stacked Balls
$\Delta \sim 15 \text{ Å}$

Optical Absorption

240 280 320
Wavelength, nm

PNT
PQD

Spectrum of QD

Nature, N&V, 2010

Individual peptides  Quantum dots  Peptide nanotubes

Self-assembly  Disassembly

PNT, assembled

PQD, disassembled
Nanotechnology of Elementary Building Blocks

Elementary Building Blocks of Nanometer Size:
- Quantum confinement:
  *QD-Biomarkers and Quantum Dot Lasers*

- Asymmetric Structure And Ferroelectric Properties:
  *FE memory*
  *NanoPiezo Devices*

- Organic Charge Storage Memory For flexible Electronics
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- MSc Maya Yevnin - Wettability

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Prof. A. Gruverman, University of Nebraska-Lincoln

Optical studies (SHG)
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Peptide Nanotubes: Peptide Flower

Thank you for your attention