Nanoscale photonic devices fabricated using DNA nanostructures

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Outline

- Background
- Motivation
- Statement of Work
- Experimental
- Results
- Discussions
- Summary & Future Work
What are photonic devices?

- Use light to perform functions
  - Fast response → picosecond
  - Wireless → high density

- An example is silicon photonics
  - Illustration of traffic routing
  - Nanophotonic switches - on-chip optical network
  - Less than 2 ns response; temperature-insensitive

Optical circuit
Another approach – DNA-based photonics

How is it made?
  ⇒ DNA as scaffolds
  ⇒ Light emitting nanostructures

What’s been done?


DOI: 10.1021/ja1105464 2011
Benefits of DNA-based -versus- silicon-based photonics

- Molecular programmable
- Predictable structures
- Self-assembly
- Light emitting nanostructures can be placed less than 10 nm

“smart” or “functional” structure = DNA + nanoparticles

Nano Letter, 2010, 10 (9), pp 3367–3372
To design and fabricate photonic devices using \textit{nанопarticle-decorated DNA nanostructure devices}, and investigate the device’s operation by optical means.
Light emitting nanostructures

- Chromophore, fluorophore, or fluorescent dye
- Absorb energy of a specific wavelength
- Re-emit energy at a different (but equally specific) wavelength
- In most cases, emitted light has a longer wavelength, and therefore lower energy, than the absorbed light.
Fluorescence resonance energy transfer (FRET)

- Non-radiative dipole-dipole coupling between two chromophores
  - Spectral overlap
  - Interchromophoric distance <10 nm
- "Near-field communication"

\[ E = \frac{1}{1 + \left( \frac{r}{R_0} \right)^6} \]

- \( E \): coupling efficiency
- \( r \): distance between donor and acceptor
- \( R_0 \): Forster radius
FRET

No Communication → No FRET

Communication → FRET
Experimental Approach

- Synthesis DNA
  - DNA tiles
  - DNA origami nanotubes

- DNA origami folding

- Chromophore selection

- Design DNA nanostructures with chromophores
  - DNA tiles
  - DNA origami nanotubes

- Synthesis DNA
  - DNA tiles with chromophores
  - DNA nanotubes with chromophores

- Experimental characterization
  - Optical spectroscopy
  - AFM
DNA Tiles – Need 2 different strand types

- **Type 1**: DNA “Scaffold Strand”
  - **Length**: ~42 nucleotides
  - **Made by**: man-made
  - **Sequence Known**: Yes
  - **Random sequence**: No

- **Type 2**: DNA “Staple strand”
  - **Length**: ~42 nucleotides
  - **Made by**: man-made
  - **Sequence Known**: Yes
  - **Random sequence**: No
DNA Origami Nanotubes – Need 2 different strand types

- **Type 1**: DNA “Scaffold Strand”
  - **Length**: 7249 nucleotides
  - **Made by**: bacteriophage
  - **Sequence Known**: Yes
  - **Random sequence**: Yes

- **Type 2**: DNA “Staple strand”
  - **Length**: ~42 nucleotides
  - **Made by**: man-made
  - **Sequence Known**: Yes
  - **Random sequence**: No
DNA origami folding

Borrowed from Paul Rothemund website
Chromophore selection

- 6-carboxyfluorescein (FAM) – primary donor

- Carboxy-tetramethyl-rhodamine (TAM) – primary acceptor
  *plus* secondary donor

- Cy5 – secondary acceptor
DNA tile design

- DNA tile
  - Each strand contains 42 nucleotides
  - 3 double helices (6x14 nm²)

- Decorated with dyes
  - A linear chain of chromophores
  - Interchromophoric distance ~2.38 nm
DNA origami nanotube design

Mathieu et al., Nano Lett., 2006, 5, 661

6-helix bundle DNA origami nanotube resembles a parallel array of six double helices

170 staple strands

Staple Motif

6 nm

412 nm

2 nm
Decorated with dyes

- A chain of chromophores
- Interchromophoric distance ~ 3.1 nm
  - 2.38 nm in x-axis
  - 2 nm in y-axis

DNA origami nanotube design

Helix Column

19 20 21
F T C

1 2 3

4 5 6

7 8 9

... ...

170 staple strands

M13 scaffold
**Synthesis process**

10x synthetic DNA  +  1x Mg^{2+} buffer  \rightarrow  DNA tiles

10x synthetic DNA  +  1x M13mp18  +  1x Mg^{2+} buffer  \rightarrow  DNA origami nanotubes

**Resulting Solution:** Nanotubes/Tiles + Excess DNA strands
Filter DNA

- Gel electrophoresis
  - Size and charge separation
- Control samples on lane 1 to 6
- Desired photonic devices on lane 7

Nanotubes/Tiles + Excess DNA strands

Nanotubes or Tiles

Excess DNA strands
Experimental Characterization

- Spectrophotometry

- Atomic force microscopy (optional)
Reminder - FRET

No Communication = No FRET

Communication = FRET
Results - Tile

- Directly excite FAM at 480 nm, TAM excitation is negligible
  - Spectral overlap & interchromophoric distance ~ 2.38 nm

Expect

Actual

Success!
Results - Tile

- Directly excite FAM at 480 nm, Cy5 excitation is negligible
  ⇒ No spectral overlap & interchromophoric distance ~ 4.76 nm

Expect

Actual

Success!
Directly excite at 480 nm, TAM and Cy5 excitation are negligible

⇒ Spectral overlap & interchromophoric distance ≈ 2.38 nm
Results - Tile

- Directly excite FAM at 480 nm, TAM and Cy5 excitation are negligible
  ⇒ Spectral overlap & interchromophoric distance ~ 2.36 nm

Expect

Actual

Success!
Performance of FRET on DNA tile

ENERGY TRANSFER Determination - FAM to Cy5

- Least-square Curve Fitting Method: 28%
- Emission Peak Method: 36%
- Single Molecule Microscopy: *have not performed*
Results - Nanotube

- Directly excite FAM at 480 nm, TAM excitation is negligible
  ⇒ Spectral overlap & interchromophoric distance ~ 3.1 nm

Success!
Results - Nanotube

- Directly excite FAM at 480 nm, Cy5 excitation is negligible
  ⇒ No spectral overlap & interchromophoric distance ~ 6.2 nm

Expect

Actual

Success!
Results - Nanotube

- Directly excite at 480 nm, TAM and Cy5 excitation are negligible
  - Spectral overlap & interchromophoric distance ~ 3.1 nm

Expect

Actual

![Fluorescence vs Wavelength](image1)

![Fluorescence (a.u./[c])](image2)

Success!
Directly excite FAM at 480 nm, TAM and Cy5 excitation are negligible

⇒ Spectral overlap & interchromophoric distance ~ 3.1 nm

Expect

Actual

Success!
Performance of FRET on DNA origami nanotube

ENERGY TRANSFER Determination - FAM to Cy5

- Least-square Curve Fitting Method: 25%
- Emission Peak Method: 36%
- Single Molecule Microscopy: *have not performed*
Performance of FRET on DNA nanostructures

ENERGY TRANSFER

- Emission Peak Method: Quake et al. reported ~ 40%
- Single Molecule Microscopy: Tinnefeld et al. reported ~ 36%

The difference could be attributed to

- Spectroscopy techniques
  ‡ (e.g. ensemble fluorescence vs. single molecule)
- Least-square analysis
  ‡ (e.g. emission peak vs. emission spectrum)
- Different buffer conditions, pH, DNA sequences
Summary

- Shown successful photonic energy transfer with “organic nanoparticles” on DNA nanostructures.
- Can this be done with “inorganic nanoparticles” (e.g., semiconductor quantum dots)?
  - Experimental approach
    - Same approach with dyes on nanotubes
    - Replace dyes with QDs

Success!
Thank You
$S(\lambda) = f \, F(\lambda) + tT(\lambda) + cC(\lambda)$
AFM – Nanotubes with dyes
Förster radius is the distance at which the energy transfer efficiency is 50%.
(e.g. $R_0 = 4.9 – 5.5 \text{ nm}$ for FAM-TAM)

$$R_0^6 = \frac{9Q_0 \ln(10) \kappa_0^2 J}{128\pi^5 n^4 N_A}$$

$$J = \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$$

$Q_0$ : the fluorescence quantum yield of the donor in the absence of the acceptor
$\kappa_0$ : the dipole orientation factor
$n$ : the refractive index of the medium
$N_A$ : Avogadro’s number
$J$ : the spectral overlap integral
$f_D$ : the normalized donor emission spectrum
$\epsilon_A$ : the acceptor molar extinction coefficient

$$E = \frac{1}{1 + \left( \frac{r}{R_0} \right)^6}$$
DNA self-assembly

- Watson-Crick hybridization: complementary base pair recognition via hydrogen bond
- Information carrier in genetic material