# π共役高分子球体からの共鳴発光現象

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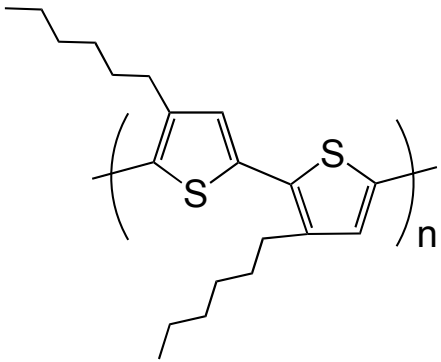
第１回 CiRfSEシンポジウム
（2015年3月13日 ＠筑波大学総合研究B棟）

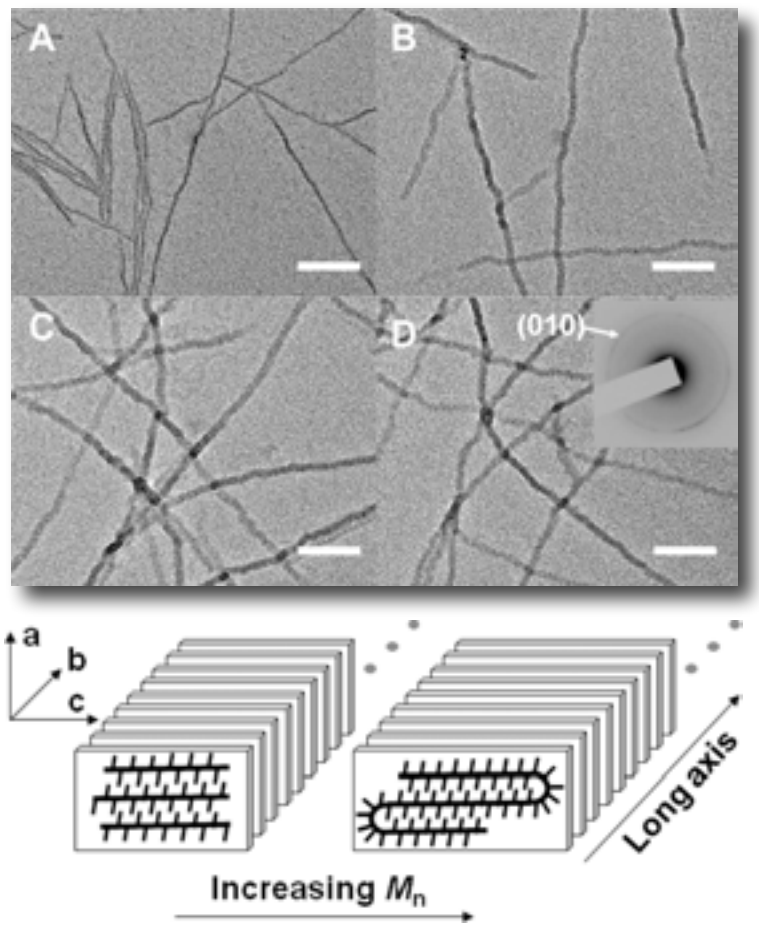
# Self-Assembly of π-Conjugated Polymers

ex) Regioregular Poly(3-hexyl thiophene)

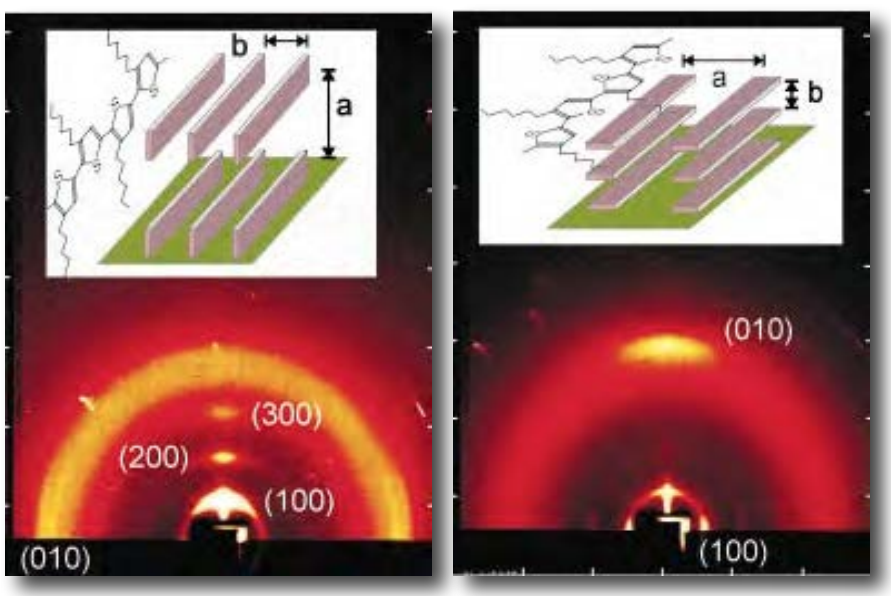
: RR-P3HT




1D Fiber




2D Sheet (Cast and Anneal)

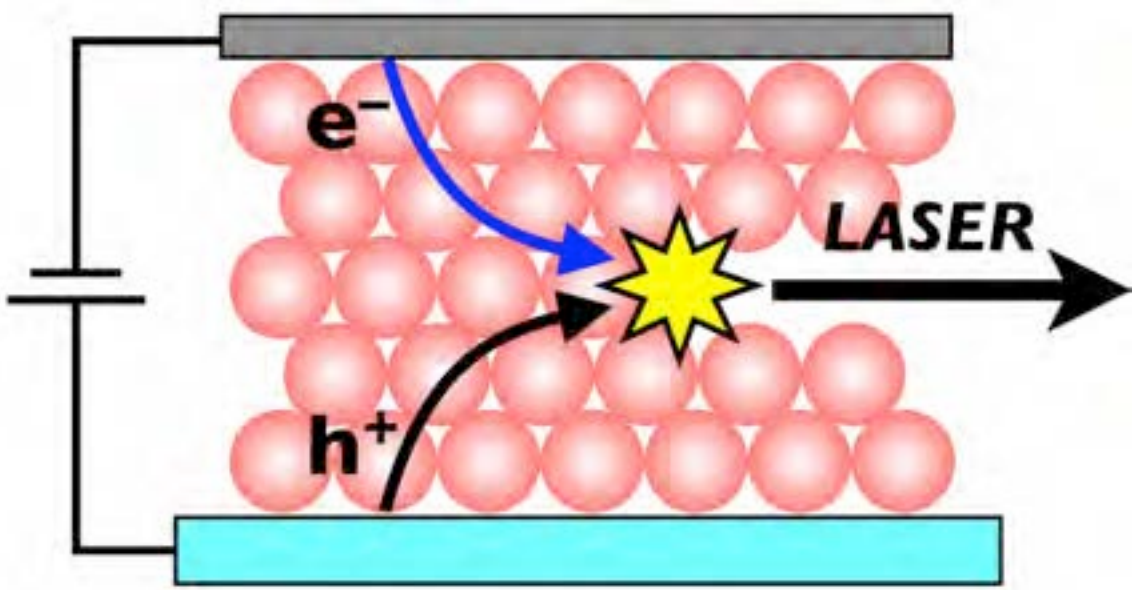



Sirringhaus *et al.*, *Nature*. **1999**, *401*, 685.

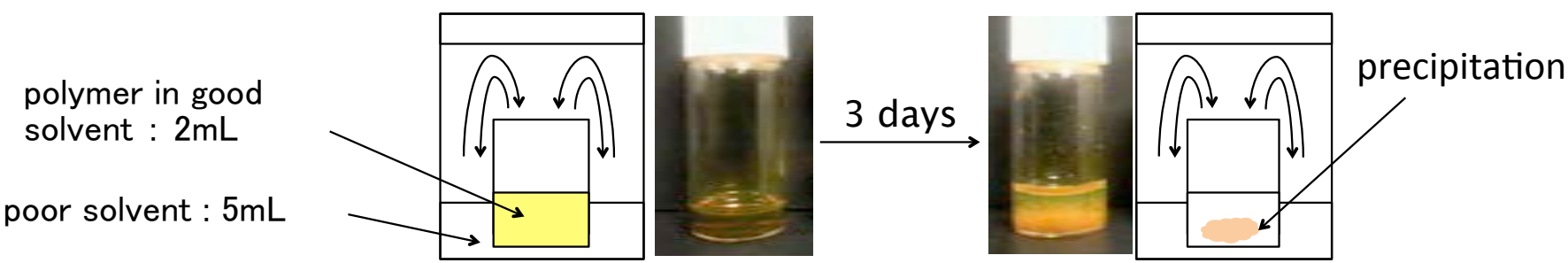
Liu *et al.*, *Macromolecules* **2009**, *42*, 9390.

# Toward Light-Emitting Photonic Crystals

No-Threshold Laser Oscillation by Charge Injection and Exciton Confinement



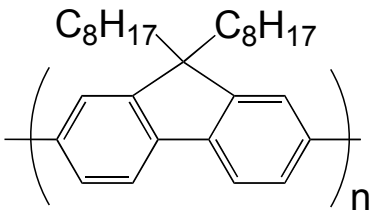

## Vapor Diffusion Method



# Single-Component Polymers

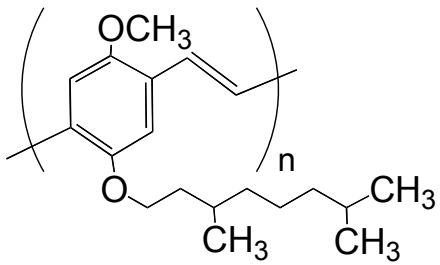
## Light-Emitting Polymers

### F8




| | $CHCl_3$ | $CH_2Cl_2$ | PhCl | THF | toluene |
|---|---|---|---|---|---|
| MeOH | × | × | × | × | × |
| hexane | – | – | × | × | × |
| acetone | × | × | × | × | △ |

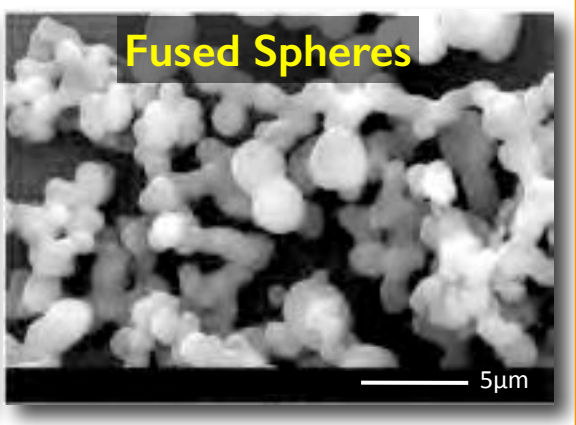
### MDMOPPV




| | $CHCl_3$ | $CH_2Cl_2$ | THF | toluene |
|---|---|---|---|---|
| MeOH | △ | △ | × | × |

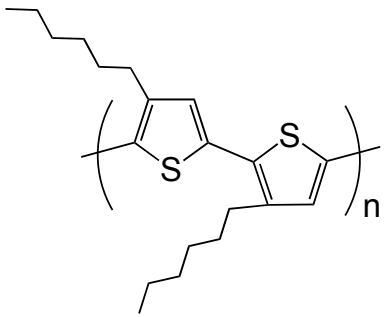
### Toluene–Acetone


### $CHCl_3$–MeOH




## Photoelectric Conversion Polymers

### regioregular P3HT

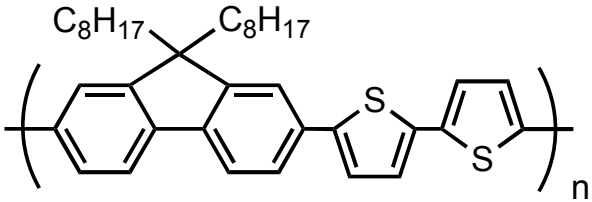



| | $CHCl_3$ | PhCl |
|---|---|---|
| hexane | × | × |
| acetone | × | × |

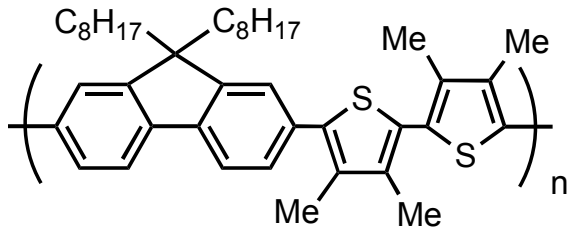
### $CHCl_3$–Hexane

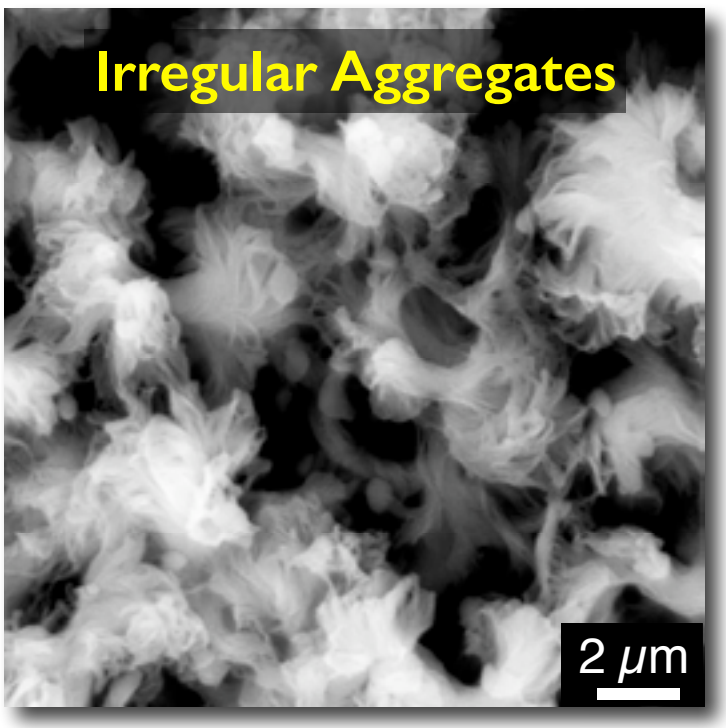
# Alternating Copolymers

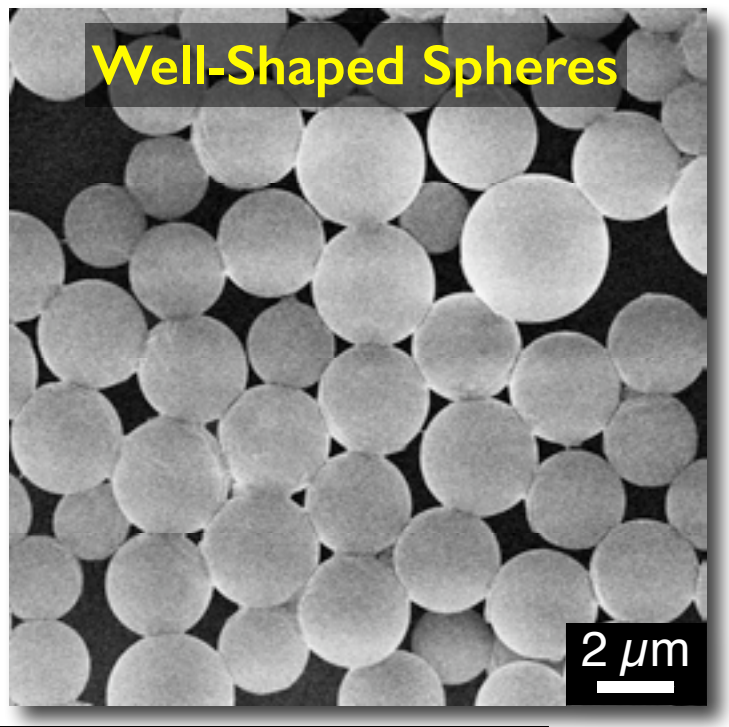
## F8T2




## F8TMT2



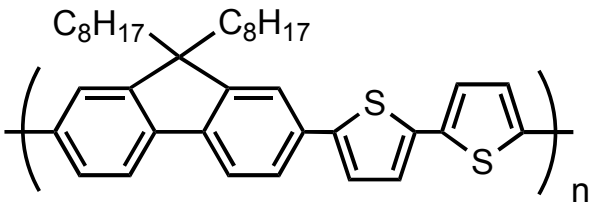

| | $CHCl_3$ | $CH_2Cl_2$ | PhCl | THF | toluene |
|---|---|---|---|---|---|
| MeOH | ◎ | ◎ | × | ◎ | × |
| hexane | — | — | — | — | — |
| acetone | ◎ | ◎ | × | △ | × |

◎: Well-Shaped Spheres
△: Distorted or Fused Spheres
×: Irregular Aggregate
—: No Precipitation

*J. Am. Chem. Soc.* 2013, *135*, 870.

# Alternating Copolymers

## F8T2

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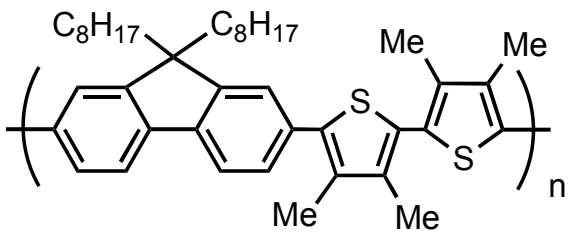
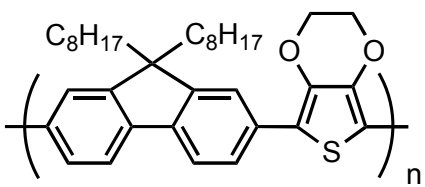
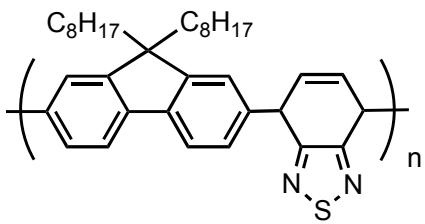


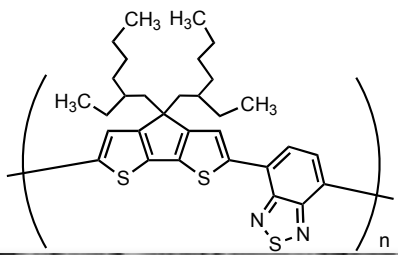

## F8EDOT

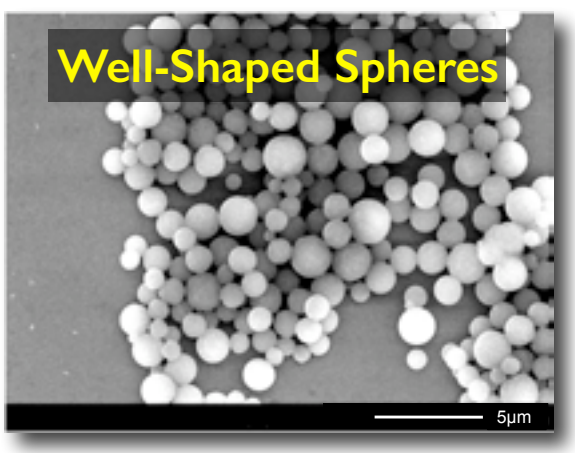


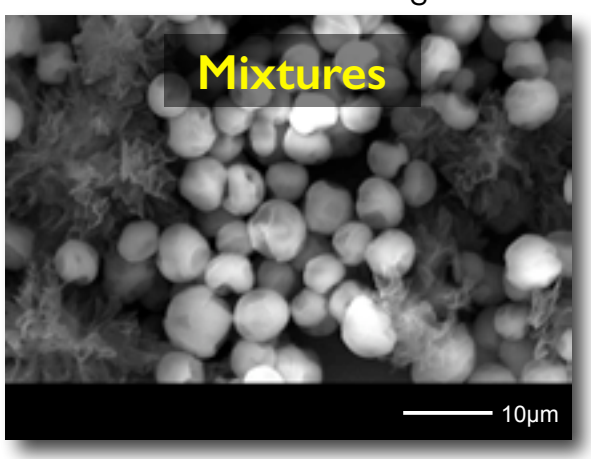

## F8BT

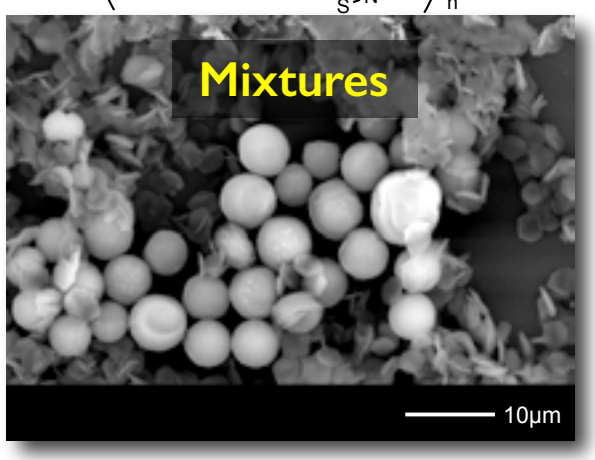



## PCPDTBT



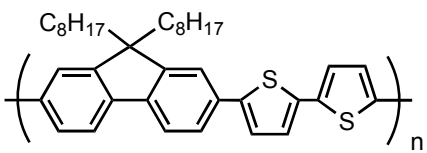

*J. Am. Chem. Soc.* 2013, *135*, 870.

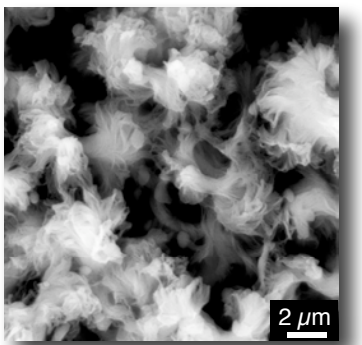
# Why Spheres Formed ?

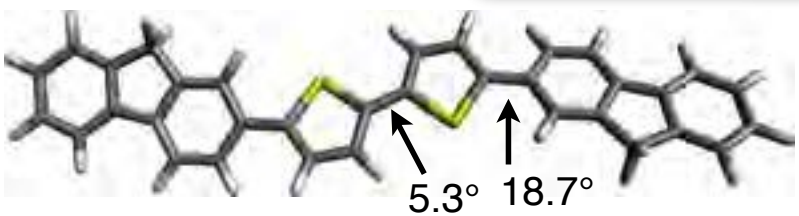
√ What kind of polymers form spheres ?

Low crystallinity is an important factor.

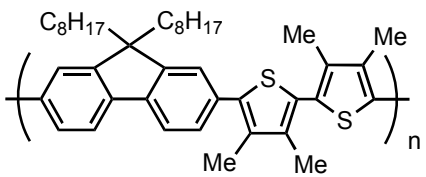
F8T2

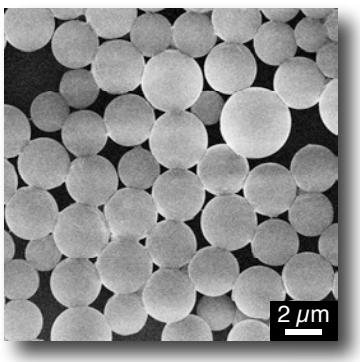


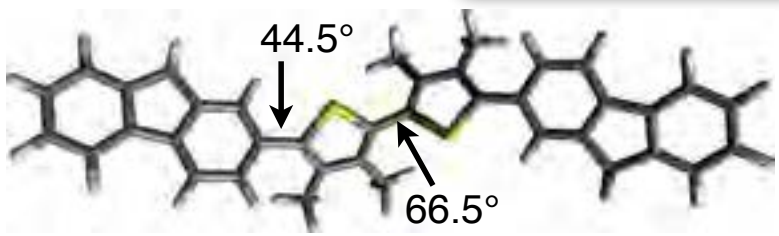




F8TMT2




√ Why spheres ?

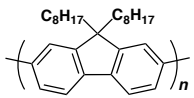
Hydrophobic alkyl chains tend to avoid contacting with polar solvents, thus forming spherical assemblies (minimal surface area).

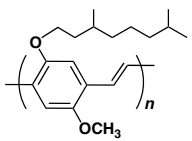
(No nonsolvent diffusion, no spheres were obtained)

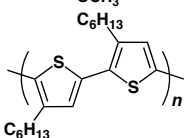
*J. Am. Chem. Soc.* 2013, *Polym. Chem.* 2014.

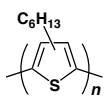
# Summary of the Spherical Formation

## Single-Component Polymers

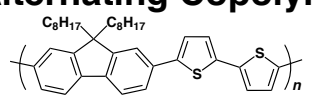

F8

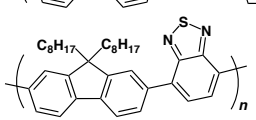

MDMOPPV


RR-P3HT


rr-P3HT

## Alternating Copolymers


F8T2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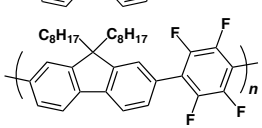
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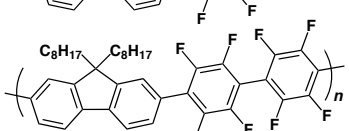
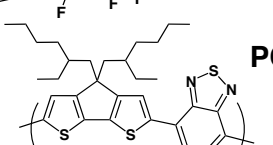
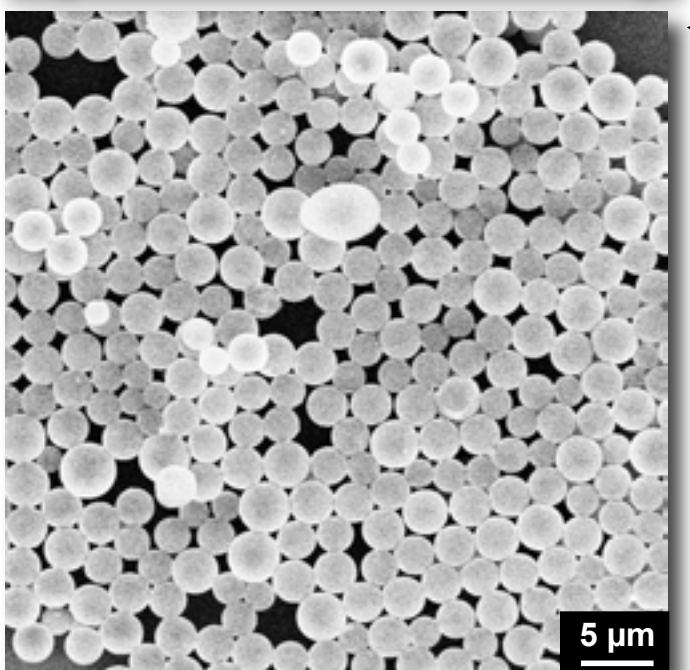
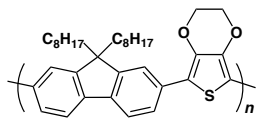

F8TP2

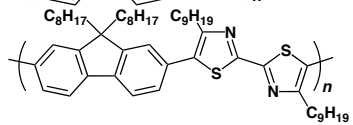

PCPDTBT

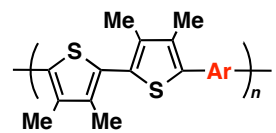
## Spherical Assembly

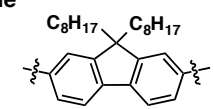


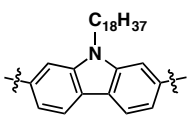

## Alternating Copolymers

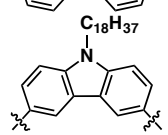

F8EDOT

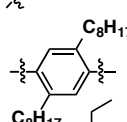

F8TAZ2

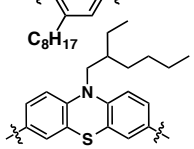

Ar-TMT2


Ar = F8


2,7-K


3,6-K


DOP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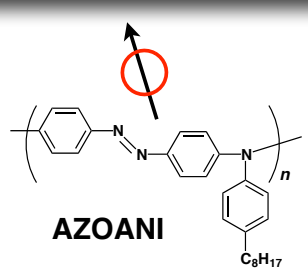
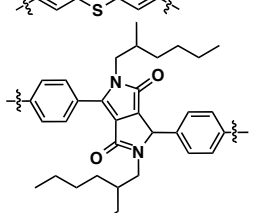
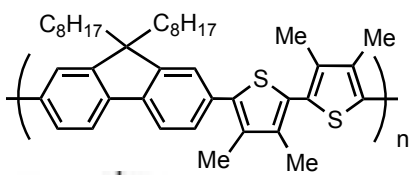

AZOANI

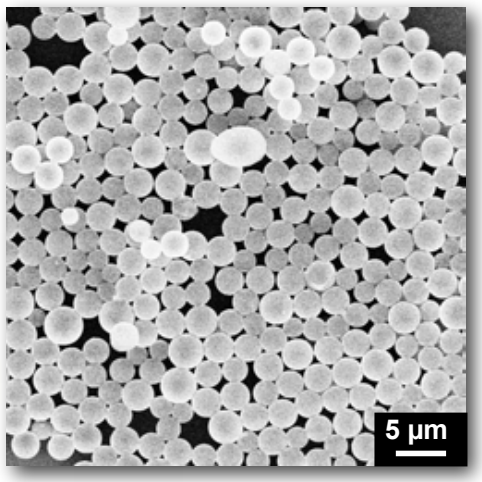

DPP

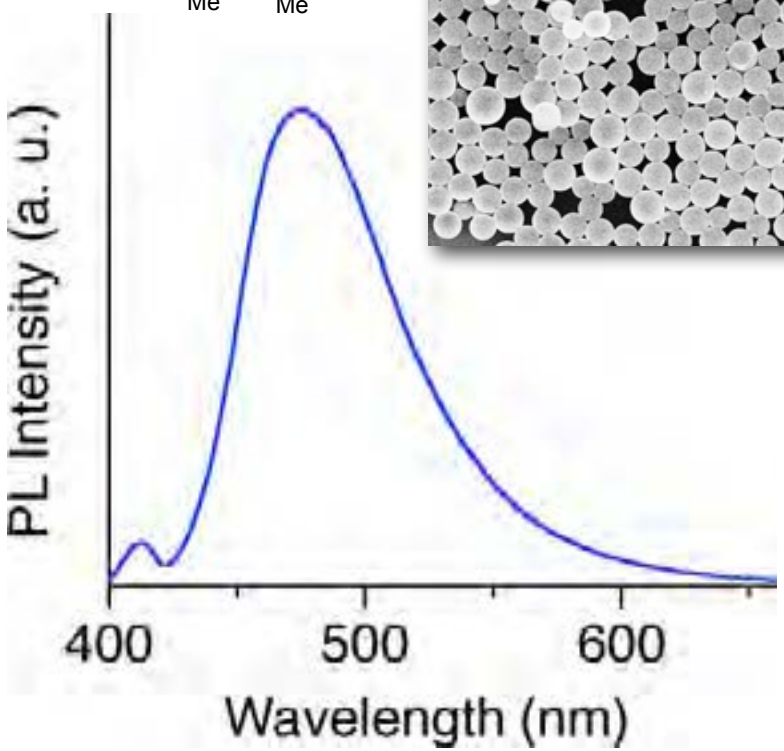
# Photoluminescence from a Single Sphere

## PL of Thin Film of Spheres

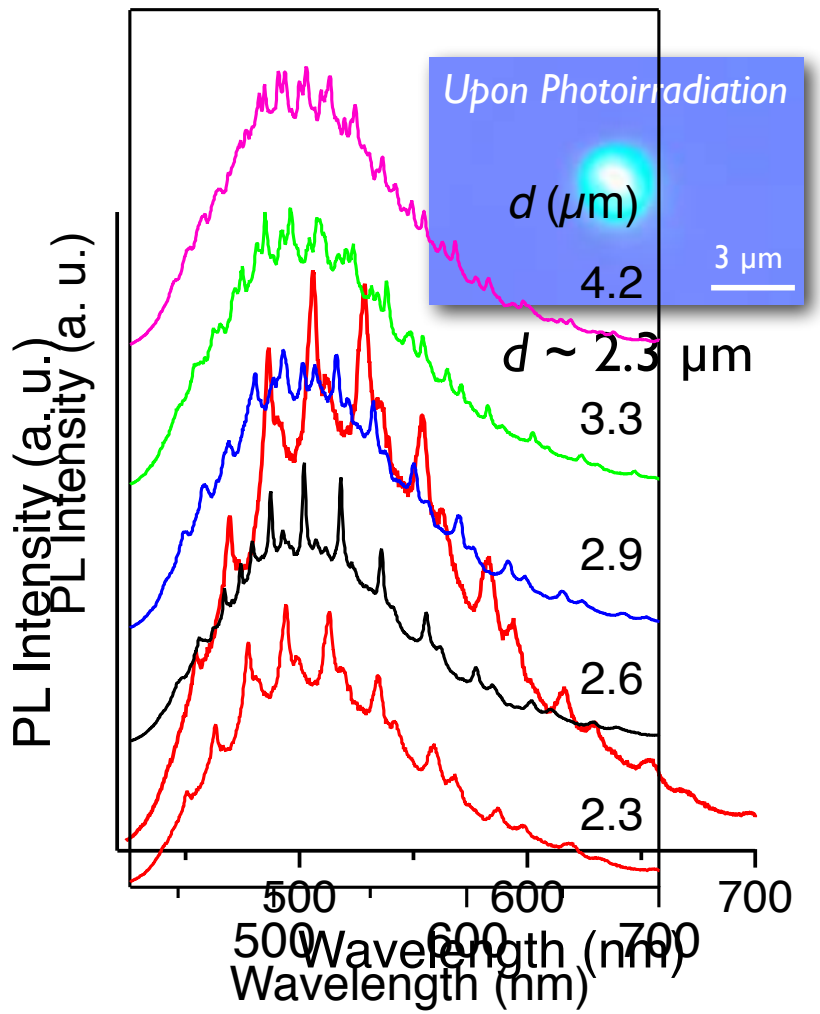
F8TMT2



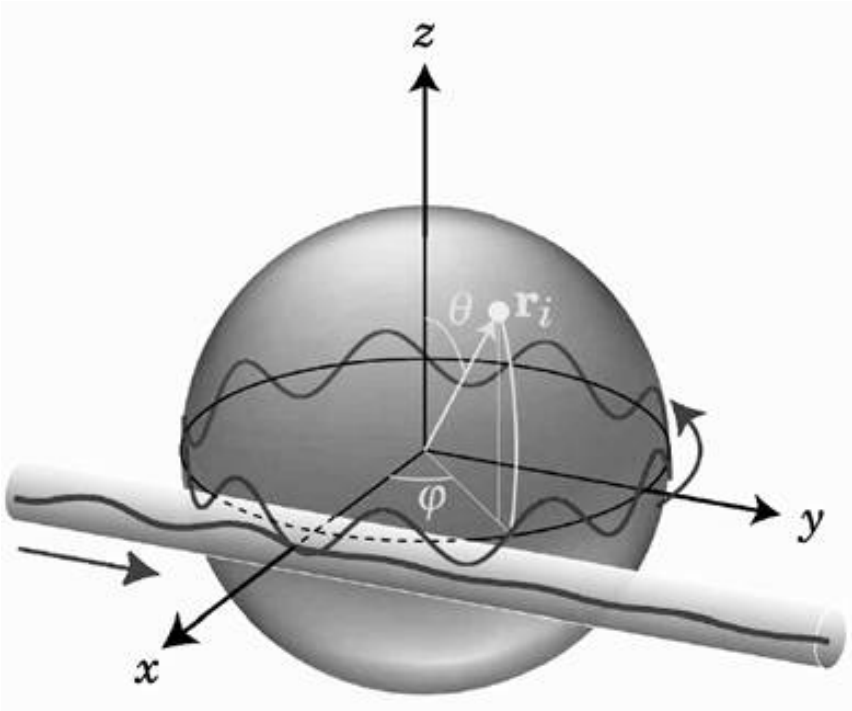




## PL of a Single Sphere

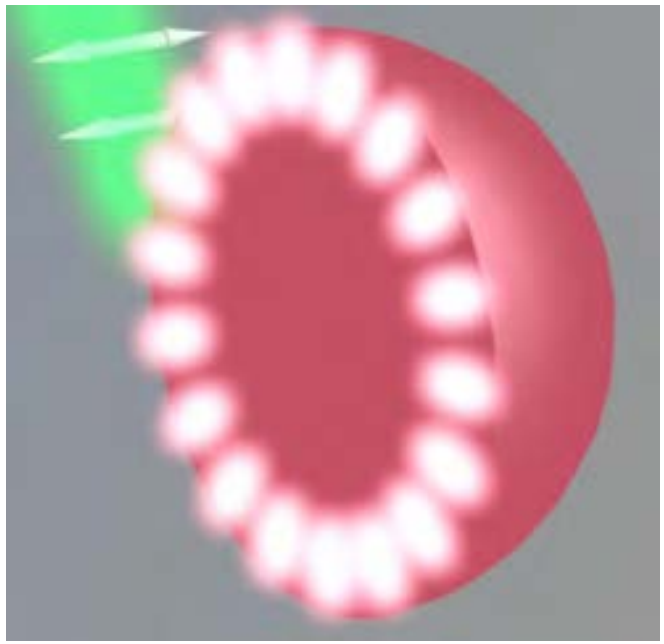



→ Whispering Gallery Mode (WGM) Photoemission

# Whispering Gallery Mode (WGM) Photoemission




Arnold *et a*l., *Opt. Lett.* **28**, 272 (2003).



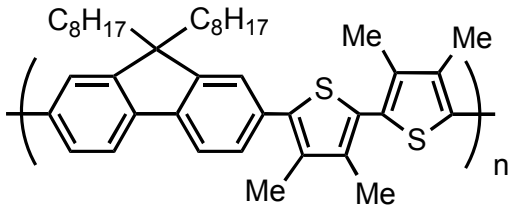
V. D. Ta *et a*l.,
*Laser &Photonics Rev.* **7**, 133 (2013).

$$\underbrace{\eta \pi d}_{\text{Optical Path}} = \lambda n$$

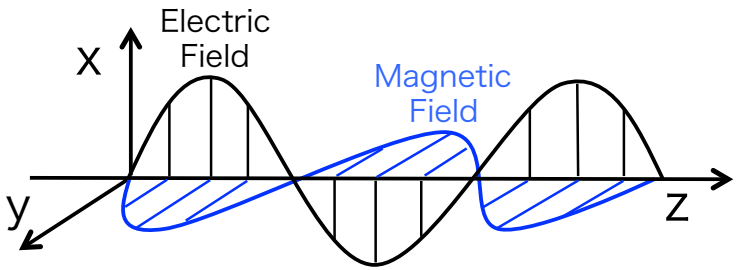
- $\eta$ : Refractive Index
- $\lambda$ : Wavelength
- $n$ : Integer Number

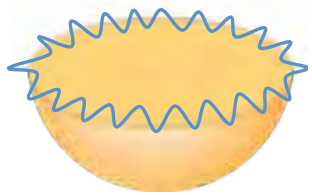
# WGM: Theoretical Simulations

F8TMT2 =

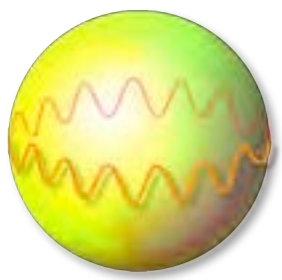



($d = 2.6\ \mu m$)

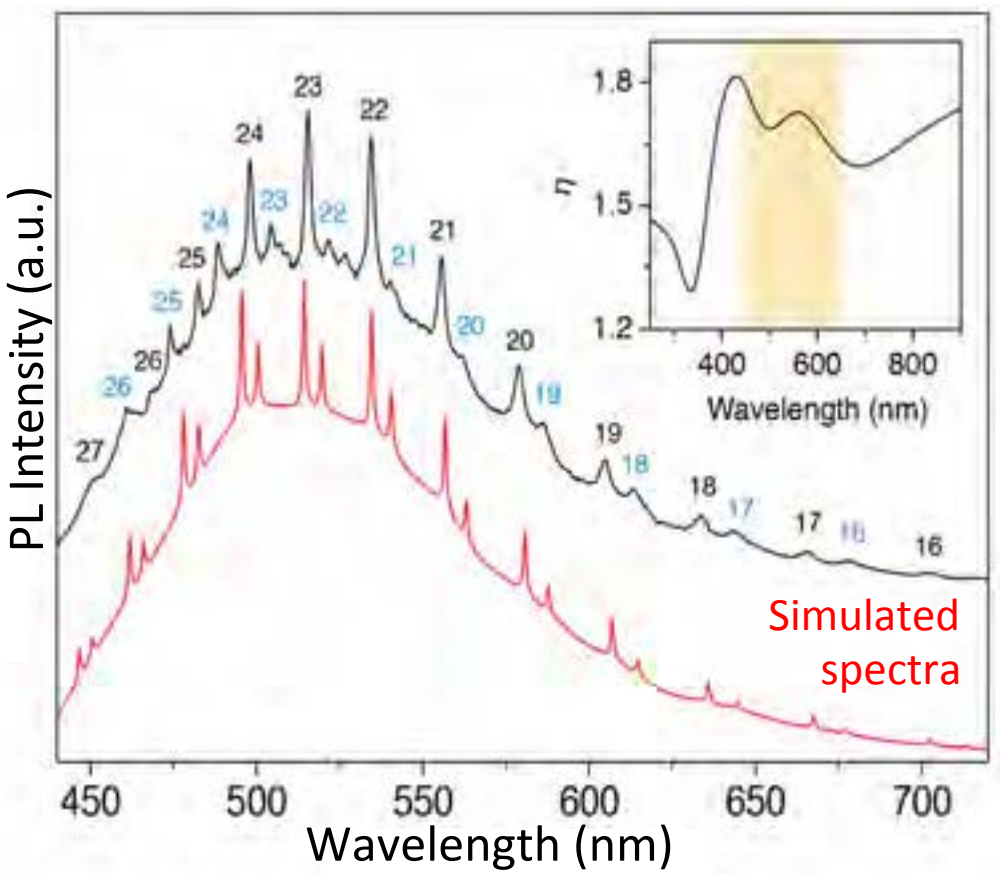


TE mode



TM mode




$$\lambda_n^E = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[(n+\frac{1}{2})+1.85576(n+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\varepsilon}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1}$$

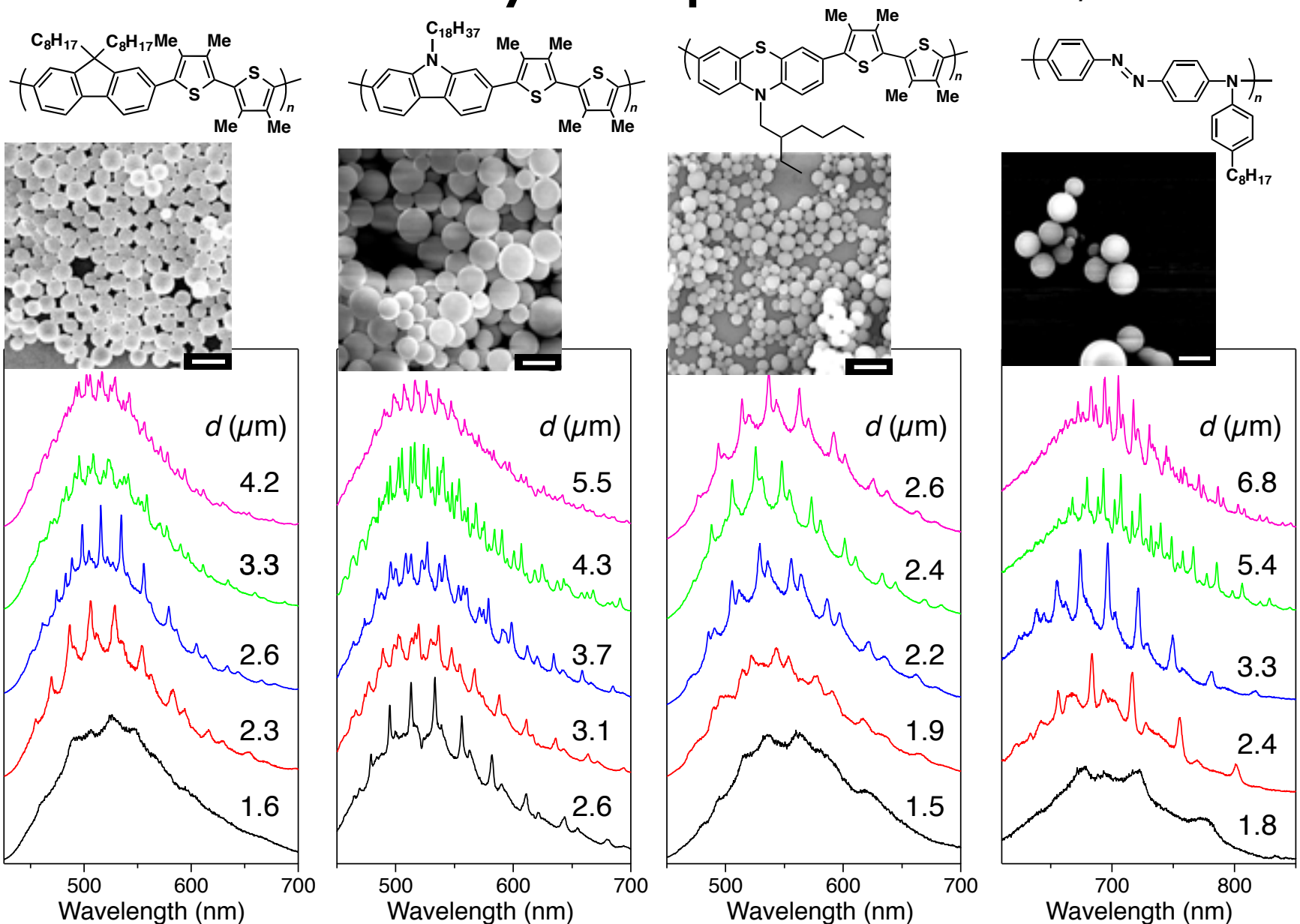
$$\lambda_n^H = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[(n+\frac{1}{2})+1.85576(n+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\mu}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1}$$

Oraevsky, A. N.; *Quant. Elect.* **2002**, *32*, 377.

*Sci. Rep.* **2014**, *4*, 5902.

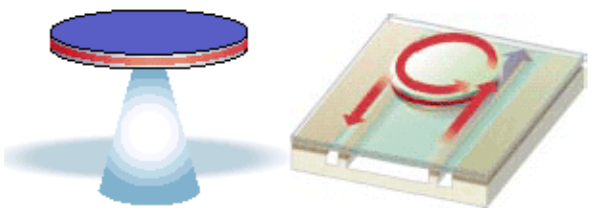
# WGM Photoemission from Various π-Conjugated Polymer Spheres

*Sci. Rep.* **2014**, *4*, 5902.



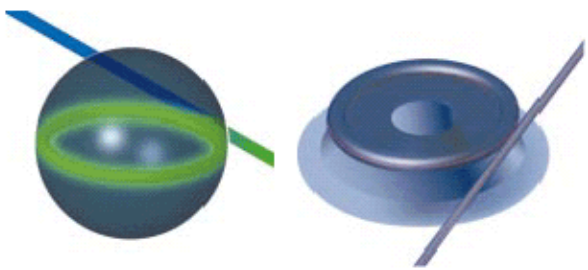
# Reports on WGM Photoemission

## Microspheres or discs by Lithography



*Q*: 12,000
*V*: 6 $(\lambda/n)^3$

$Q_{III-V}$: 7,000
$Q_{Poly}$: 1.3x10$^5$

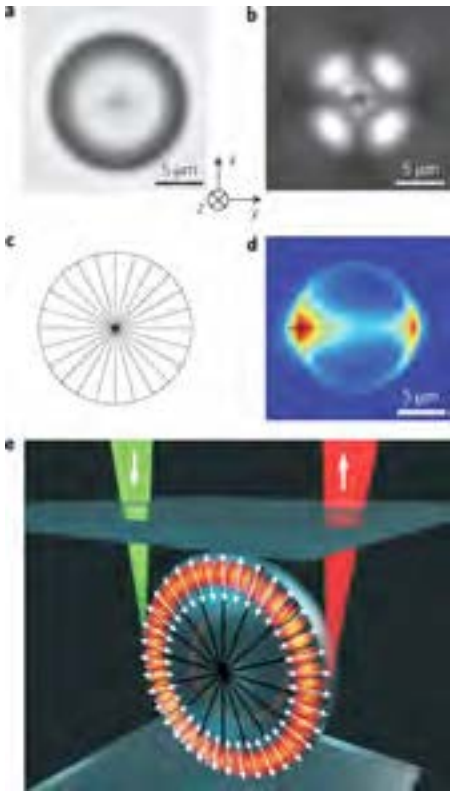


*Q*: 8×10$^9$
*V*: 3,000 μm$^3$

*Q*: 10$^8$

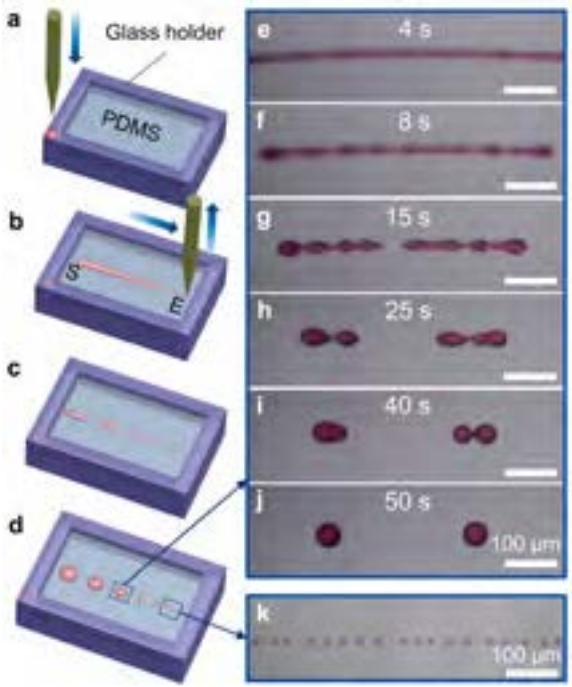
K. J. Vahala,
*Nature* **2003**, 424, 839.

## Dye-Doped Droplet of Liquid or LCs



M. Humar *et al.*,
*Nat. Photon.* **2009**, 3, 595.

## Dye-Doped Polymer Colloids




V. D. Ta *et al*,
*Sci. Rep.* **2013**, 3, 1362.

→ WGM Photoemission from a single π-conjugated polymer sphere is new !
(π-Conjugated polymer spheres act as cavity and light-emitter).

SCIENTIFIC REPORTS

*Sci. Rep.* **2014**, *4*, 5902/1–5.

OPEN

SUBJECT AREAS:
CONJUGATED POLYMERS
NANOPARTICLES

# Self-assembled conjugated polymer spheres as fluorescent microresonators

Kenichi Tabata[1]*, Daniel Braam[2]*, Soh Kushida[1], Liang Tong[1], Junpei Kuwabara[1], Takaki Kanbara[1], Andreas Beckel[2], Axel Lorke[2] & Yohei Yamamoto[1]

**本マイクロ球体の特徴**

1. 自ら**発光特性**を有する（発光色素添加が不要）
2. **高屈折**媒体（共役系高分子）
3. **共振器**としての機能（マイクロ球体）
4. **作製が容易**（微細加工技術を必要としない）
5. **電荷注入**による電界発光・電流駆動レーザーが期待できる

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Dr. Ishii

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Thank you for your attention !
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Sakuraba