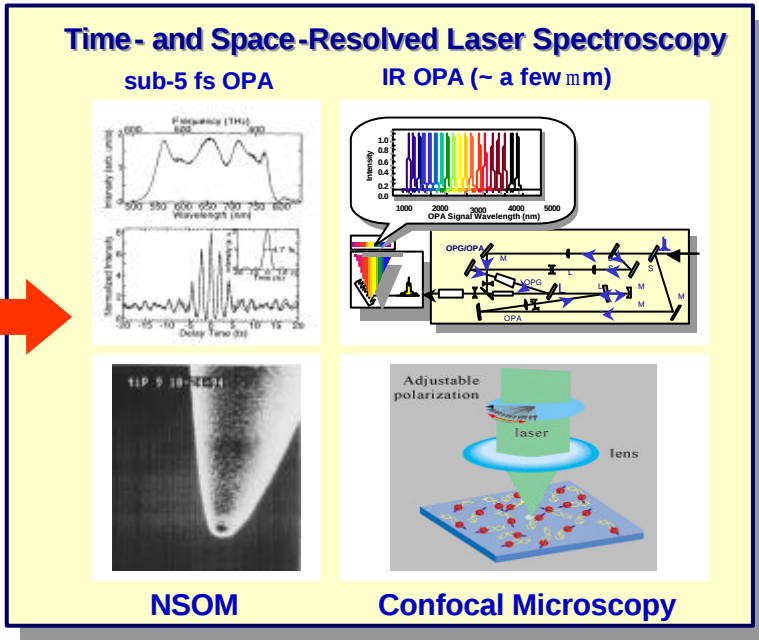
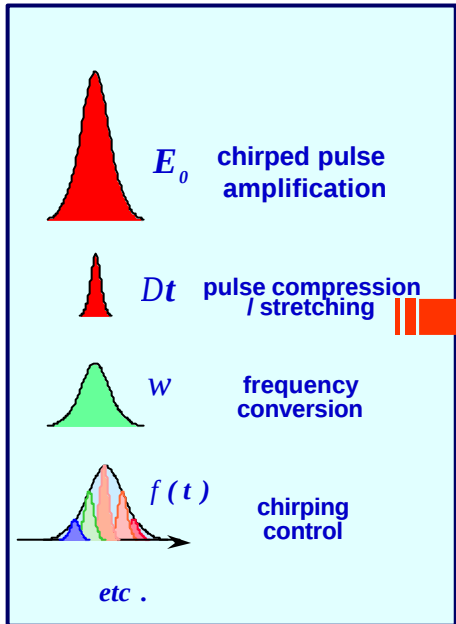


<http://chem.yonsei.ac.kr/~CUOCC>



Ultrafast Optical Characterizations Extending to *Space Domain*



nanoscale

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100 fs

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morphology

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Sub 5 femtosecond Non-collinear Optical Parametric Amplifier (NOPA) System

NOPA (Non-collinear Phase-Matched Optical Parametric

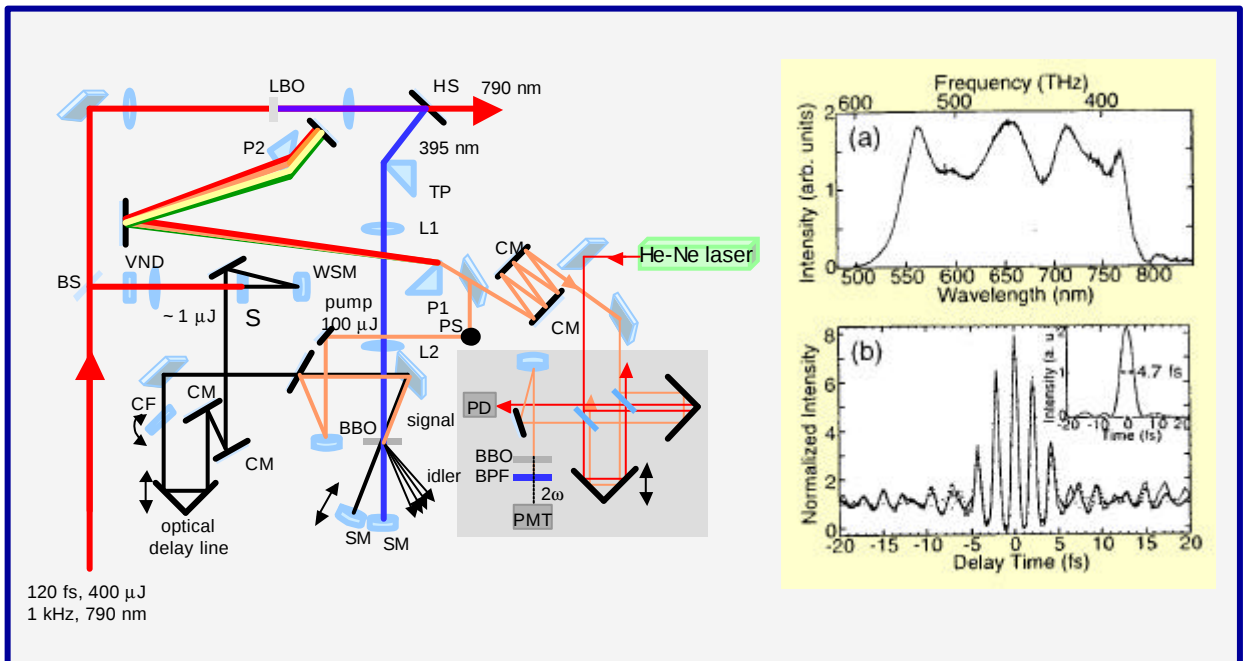
Amplifier) System 가

가

가

가가

가



beam	OPA	OPA System	white light continuum	seed -
continuum				white light
prism pair	200	broad	compression	가
nm pump beam		(β-BBO crystal)		chirped mirror set
		(Parametric Interaction)		seed beam 395
			OPA	
				(550 ~ 780 nm)
tilt	pulse front	matching	pumping beam	front
mirror set	prism pair	signal beam	200	right angle prism
		compression	5	chirped

Femtosecond Coherent Spectroscopy using Chirped Ultrashort Pulse

가

. Femtosecond Coherent Spectroscopy (FCS,

)
probe Technique

, Pump Pulse

. Pump -
Probe pulse

Transient Absorption
Fourier

Oscillatory Signal

(Raman, IR

Anisotropy

Energy Transfer

, Exciton Coupling Dynamics

5W cw Nd:YVO₄
72MHz, 100mW

(Millennia V, 532 nm)

Cavity-dumping, 200kHz, 20 mW,
800 nm, FWHM 80 nm

Fundamental Pulse (Group Velocity Dispersion)

Transform-limited Pulse 100μm BBO Crystal

400 nm FWHM 13 nm

, Beamsplitter Pump Pulse Probe Pulse

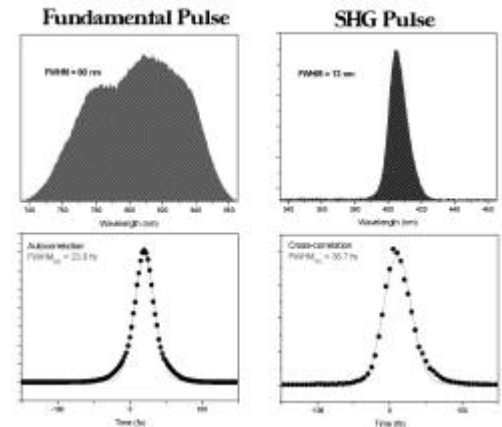
Transform-limited, Chirped Pulse . Pump Pulse

Probe Pulse 가, Chopper

Pulse Photodiode Chopper

Transient Absorption Spectrum

Characterization of Pulse



Mode-locking Ti:Sapphire Laser
Opto-acoustic Modulation

20

Compensation

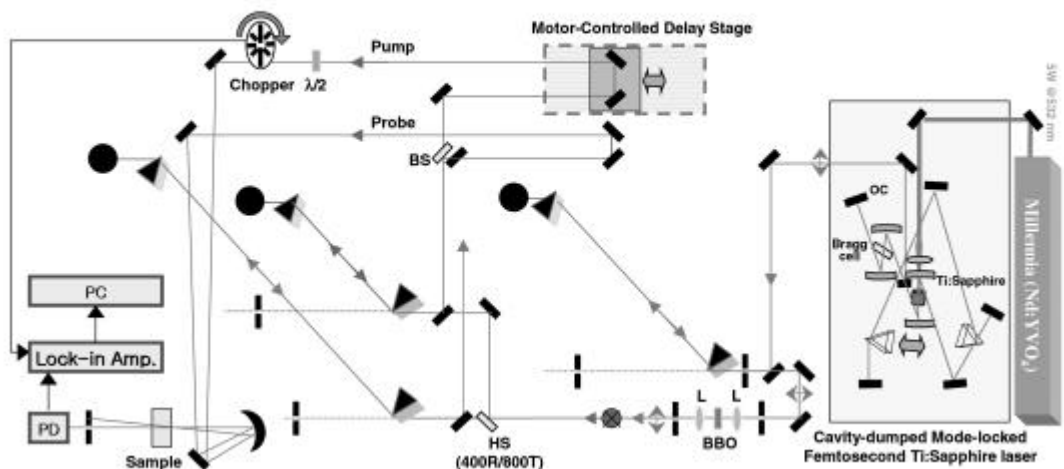
2
Compression 30 fs

Delay Stage

Probe

Lock-in Amplifier

Schematic Setup of Femtosecond Coherence Spectroscopy using Cavity-dumped Mode-locked Ti:Sapphire sub-20 fs Laser



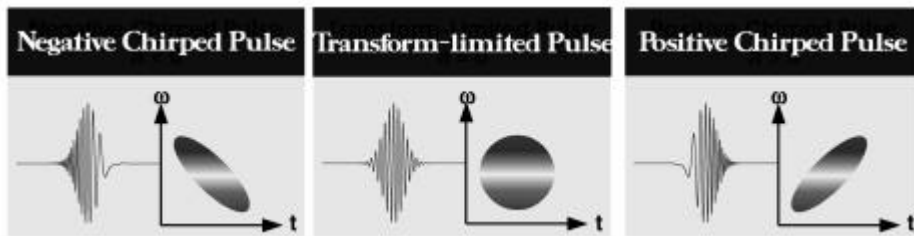
Coherent Vibrational Motion on the Porphyrin Monomers using Chirped fs Pulse

Pulse 20 가 Cavity-dumped Mode-locked Ti:Sapphire Laser , FWHM(Full-Width Half-Maximum) 80 nm 가
 800 nm 가 . ,
 (1) , w_i (1) t
 (2).

$$E = \hat{e} E_o e^{i(\omega t - \vec{k} \cdot \vec{z} + f)} \dots (1)$$

$$w_i = \frac{d}{dt}(\omega t - \vec{k} \cdot \vec{z} + f) \dots (2)$$

$w_i = \omega$ 가 , 가 Transform-limited Pulse .

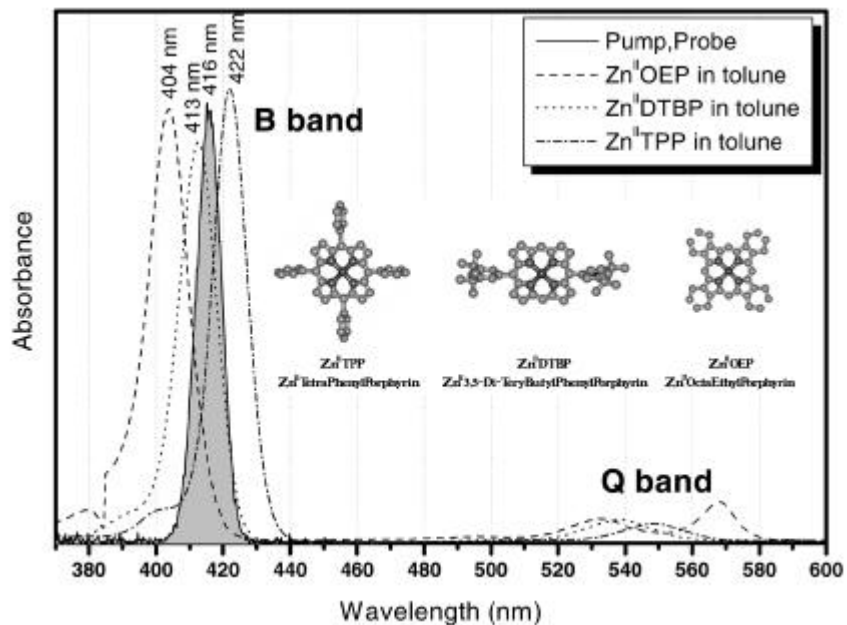


$w_i = \omega + 2at$ 가 , Linearly-chirped Pulse . Chirped Pulse 가 , 가
 Positively-Chirped Pulse . Chirping Control Laser Pulse Compression Prism
 가 가 Shaping

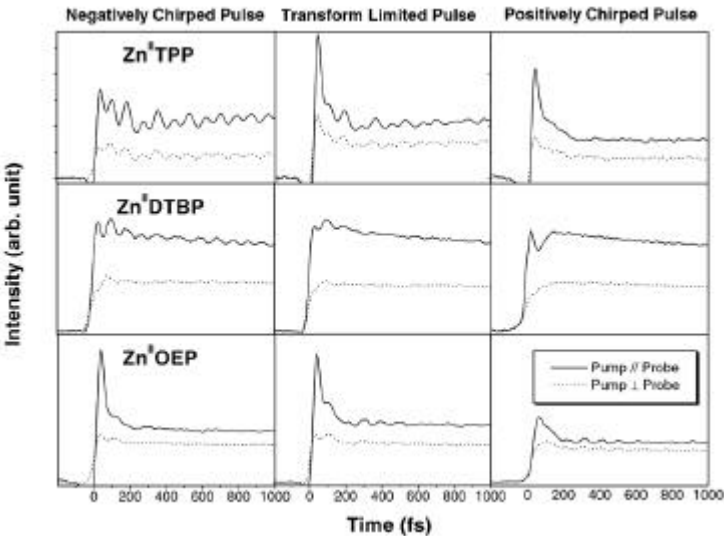
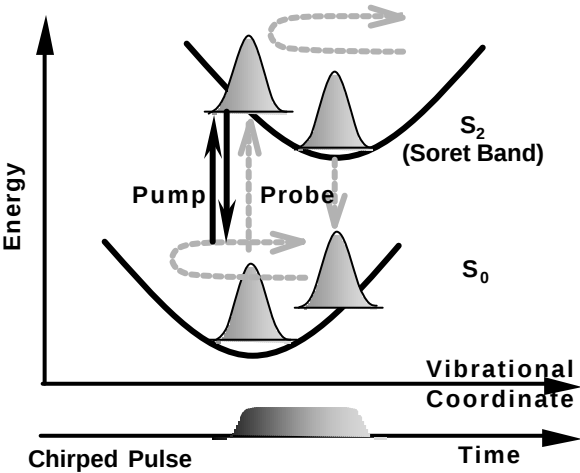
Device Molecular Opto-electronic
 Molecular wire 가
 array

Zn^{II}TPP, Zn^{II}OEP, Zn^{II}DTBP
 Soret Band (B band) Pump-probe
 Technique Transient
 Absorption .
 Porphyrin

가 .
 400nm Soret Band
 Excitation . Laser Pulse
 30 Cavity-dumped
 Mode-locked Ti:Sapphire Laser
 , Pump
 Probe pulse 416 nm

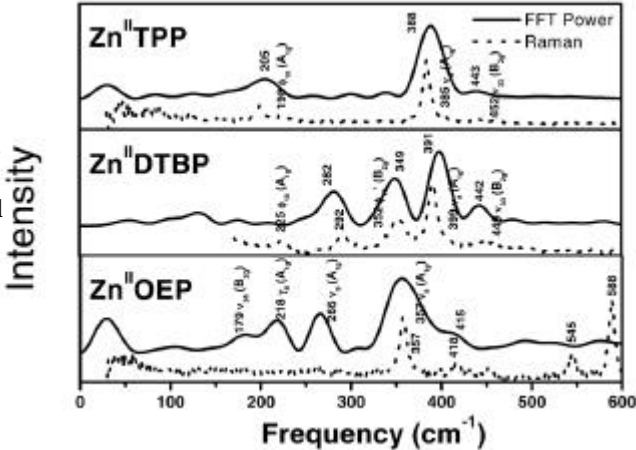


Transient Absorption
 Time-resolved Spectrum 가
 . Ground-state Bleaching, Excited-state Stimulated Emission, Excited-state Absorption
 Electronic Transition
 Coherent Vibrational Motion
 Oscillatory Signal
 Oscillation $Zn^{II}TPP > Zn^{II}DTBP > Zn^{II}OEP$
 $Zn^{II}TPP$ $Zn^{II}DTBP$ 가
 Negatively Chirped > Transform limited > Positively Chirped Pulse
 , $Zn^{II}OEP$



Potential Energy Surface(PES) , Pump Pulse
 Electronic State ($S_2 \sim S_0$) Coherent
 State가 ,
 (Wave Packet)
 Pulse Excited Ground State
 PES ,
 Excitation $Zn^{II}TPP$ $Zn^{II}DTBP$
 가 Negatively Chirped Pulse
 가 PES
 가 Dephasing
 Chirped Pulse , Positively
 Oscillation Dephasing
 Oscillation $Zn^{II}OEP$
 Excitation

Oscillatory Part Fourier Transform
 Power Spectrum ,
 Power Spectrum
 Ground State Resonance
 Raman Spectrum
 $Zn^{II}OEP$ 200 cm^{-1} Raman
 가 FCS , Ground
 State Excited State
 Excited State 가
 Transition Electronic State
 가
 Energy Transfer , Electronic State
 가
 $Zn^{II}TPP$ $Zn^{II}DTBP$ 가 Candidate 가 가

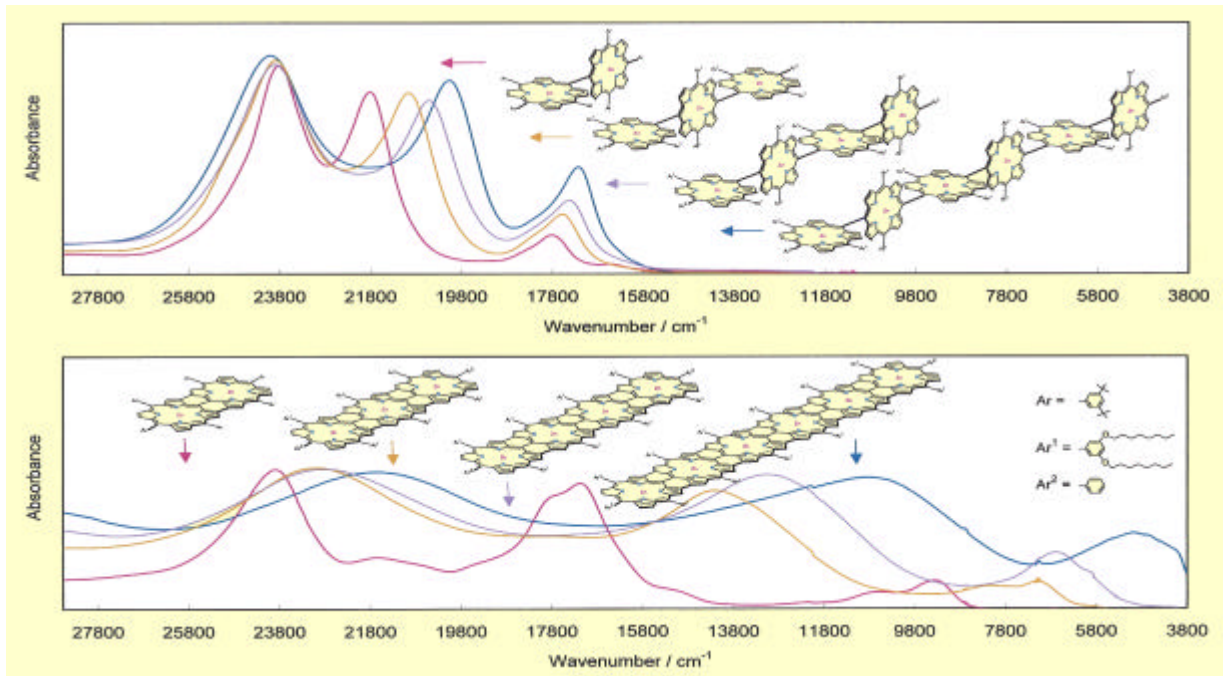


Photophysics of Porphyrin Molecular Wire as Photonic Devices

가

가

π - (conjugation) fused



1.

fused

1

가

가
가
(coherent length)가 “
가”

가 108 nm가

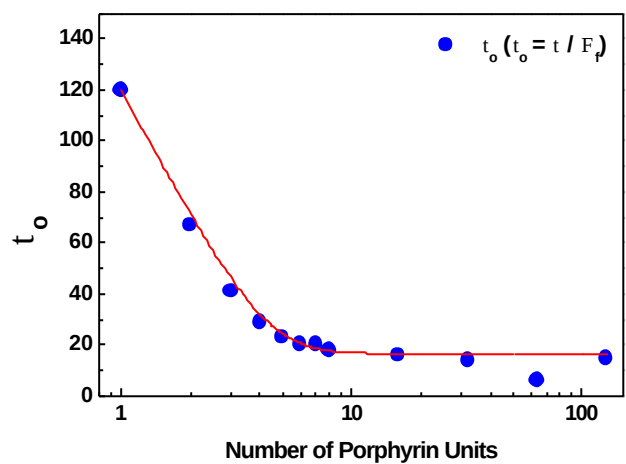
128

(natural radiative lifetime)

5-6

가 4

2



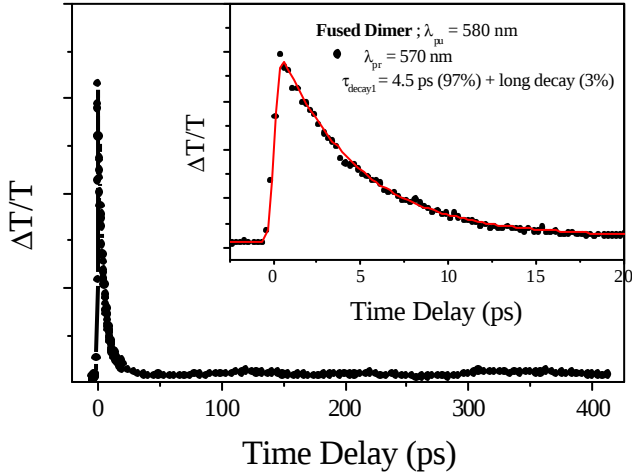
2.

(relative natural radiative lifetime)

가
(conjugation saturation)

Q-band

conjugated length)가



3. 2.1 eV

fused

bleaching recovery

4 B- (3.1 eV)

bleaching recovery
(1.2, 2.2 eV)

2.9 eV

bleaching rise가

bleaching rise가

fused

Q-

pathway가
가

(B-)
bottle-neck

Fused

12

fused

2500 cm^{-1}

가

1

가

(effective

fused

가

3

(2.1 eV)

recovery

(~4.5 ps) bleaching recovery

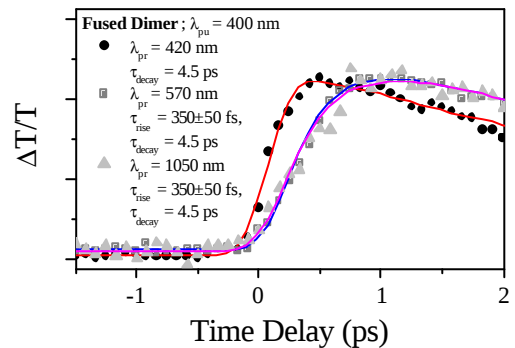
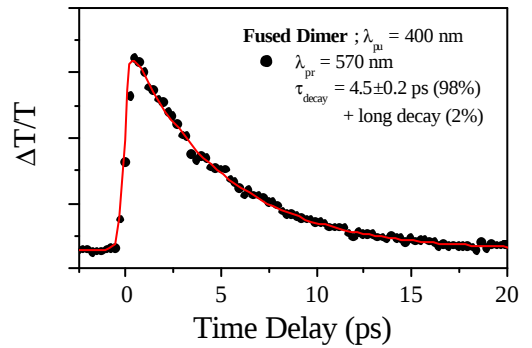
(1.2, 2.9 eV)

bleaching recovery

1.9 ns

bleaching recovery

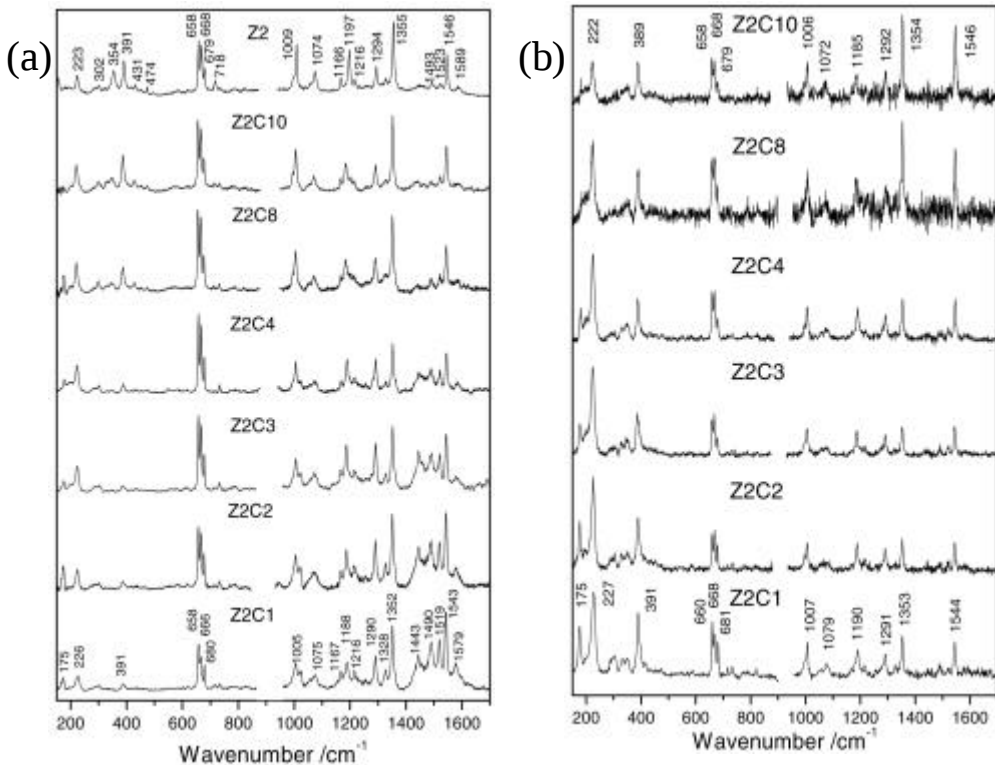
가



4. 3.1 eV

fused

bleaching recovery.



3. Strapped Porphyrin Dimers Resonance Raman Spectra.
 (a) 458 nm excitation. (b) 488 nm excitation.

Exciton Theory

π - π interaction

, Strapped Porphyrin

Dimer
가

Porphyrin Ring

Strapped Porphyrin Dimer

Dimer
MO

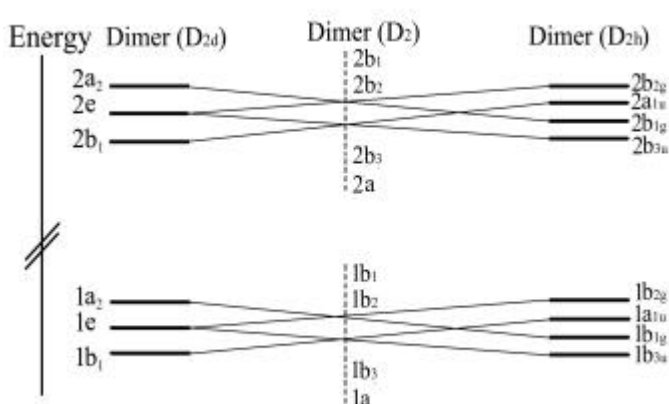
Molecular Orbital

Supermolecular MO Approach

. Supermolecular
four orbital theory

Goutermann four orbital basis function

가 Strapped Porphyrin Dimer MO



4
0 (D_{2h})
90 (D_{2d})
MO
Super-
molecular MO
configuration interaction
Strapped Porphyrin Dimer
Exciton Theory
Charge
Resonance Character

4. Strapped Porphyrin Dimer Molecular Orbital

Resonance Raman Study of Directly-Linked Porphyrin Arrays

Resonance Raman Spectroscopy

Porphyrin Array
가

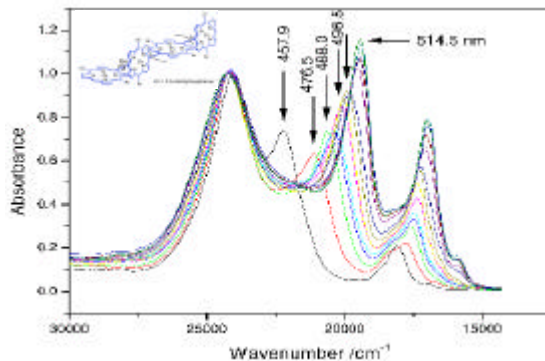
1 Porphyrin Array
Porphyrin Unit 가 가
410 nm

Exciton Band
Energy Soret band
Raman Excitation Line

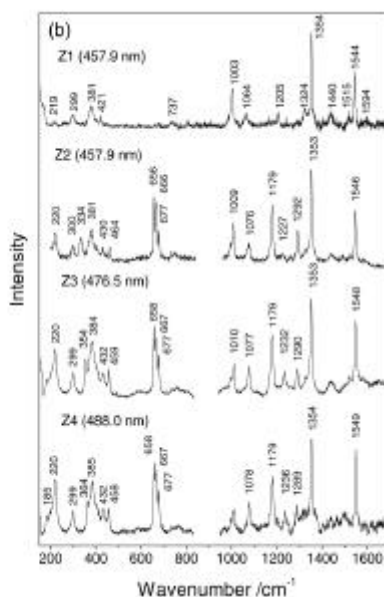
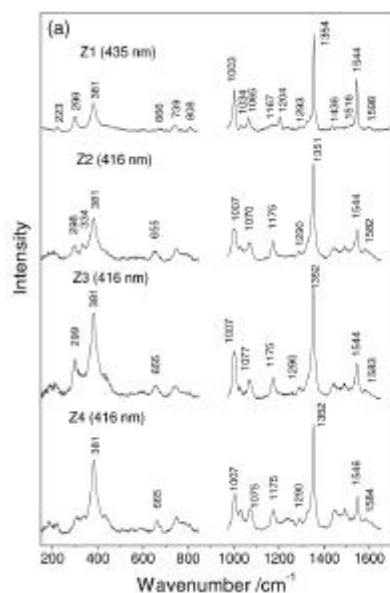
2

Directly-Linked
Soret Exciton Band
Resonance Raman

High-Energy Soret
Low-



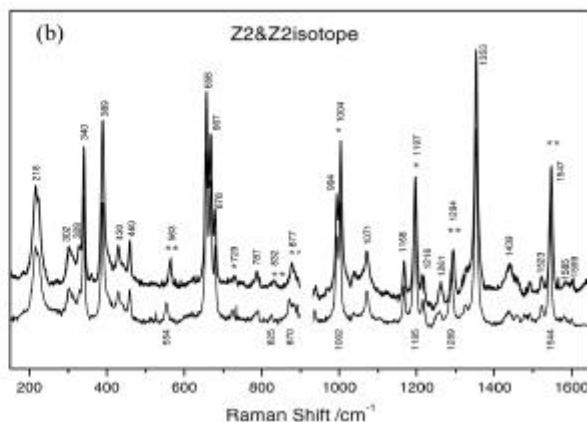
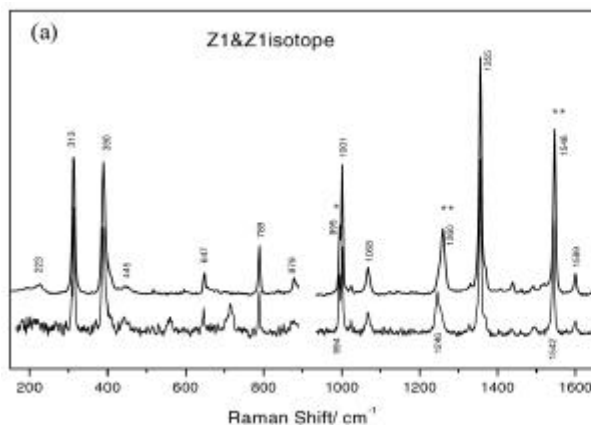
1. Porphyrin Array



Z1 ~ Z4 RR spectrum
High-Energy Soret Exciton Band
Resonance Excitation
Porphyrin Monomer Spectrum
Low-Energy Soret Exciton
Band Excitation Dimer
Symmetry Spectrum
AM1
PM3 Normal Mode
Calculation Vibration
Spectrum
Porphyrin Dimer
Dimeric Interaction
Vibrational Splitting
Splitting Mode
isotope

3

2. Porphyrin Array RR Spectrum. Excitation at High-Energy Soret Transition, (a) & Low-Energy Soret Band (b).



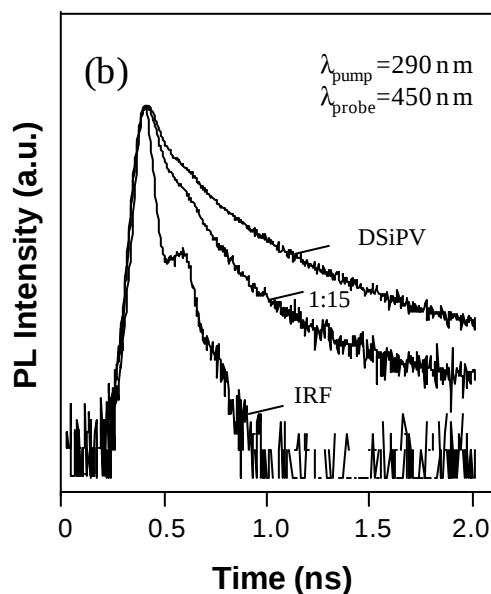
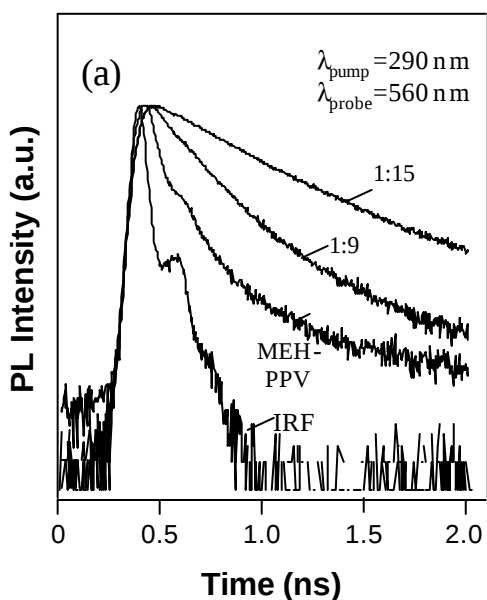
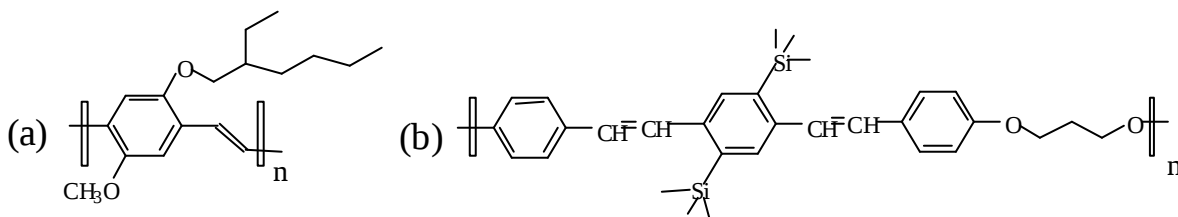
3. Isotope Experiment. (a) for Z1 & (b) for Z2.

Ultrafast Energy Transfer Dynamics of Blended Polymeric Systems

가
dipole -dipole
blending
Förster type
methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]] DSiPV (poly[1,3-propane-dioxy-1,4-phenylene-1,2-ethylene(2,5-bis(tri-methylsilyl)-1,4-phenylene)-1,2-ethylene-1,4-phenylene])
blend polymer 가 가
가

femtosecond laser
femtosecond laser
picosecond laser
fluorescence up-conversion
exciton
dipole -dipole
가

morphology (miscibility), 가



Confocal Scanning Microscope System

steady-state μm) time- resolved photoluminescence (~ ps)

Confocal Microscope

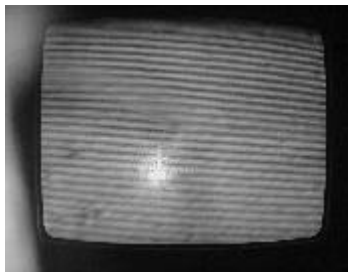
(~

5W cw Nd:YAG (Verdi, 532 nm)
Mode-Locking Ti:sapphire
laser beam splitter
Confocal Microscope

source . Trigger
CFD TAC

PMT
TAC

1200 groove/mm



×100 Objective Lens (N.A 0.9)

cw He-Cd laser(442nm, 50 mw)
590)

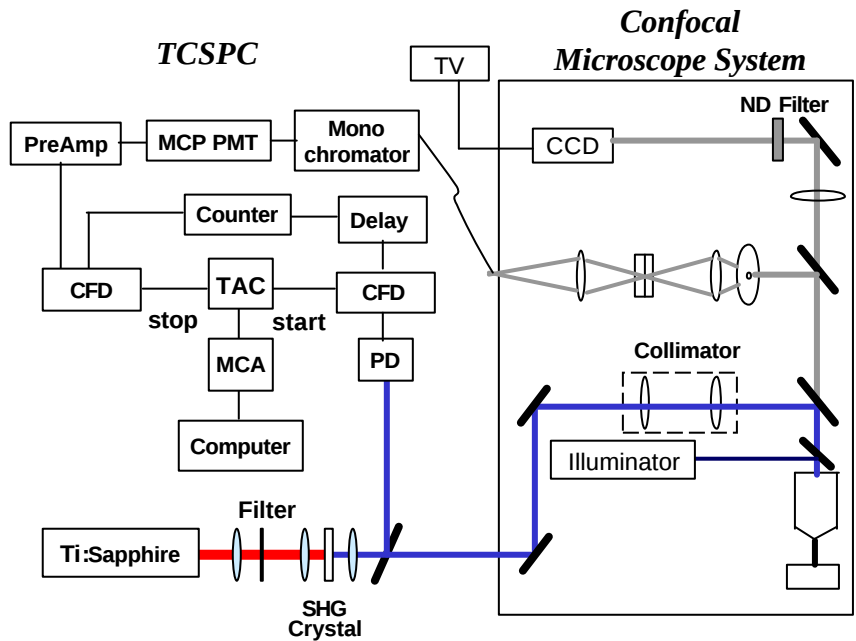
In-Focus Out of Focus
spatial filter (slit)

of Focus

(Rhodamine

Out

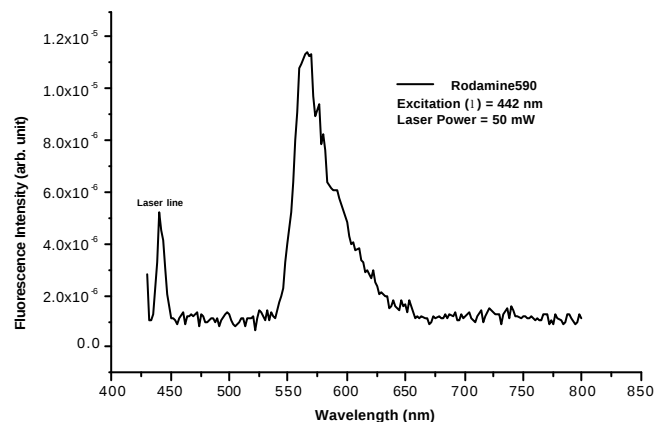
focal point



Confocal Microscope

laser(442nm)
1 μm

가
(1200 groove/mm) cw He-Cd
(*100, N.A 0.9)





Director Prof. Dongho Kim
dongho@yonsei.ac.kr



Post Doc. Dr. Dae Hong Jeong
jeongdh@alchemy.yonsei.ac.kr



Ph.D Student Cheon Min Kim
cmkim@alchemy.yonsei.ac.kr



Ph.D Student Hyun Sun Cho
hscho@alchemy.yonsei.ac.kr



Ph.D Student Jeong-Hyun Ha
hajh@yonsei.ac.kr



Ph.D Candidate Yong Hoon Kim
yhhkim@alchemy.yonsei.ac.kr



Ph.D Candidate Min-Chul Yoon
mcyoon@alchemy.yonsei.ac.kr



Grad. Student Sung Mun Jang
jangsm@yonsei.ac.kr



Undergrad. Student Jae Hong Park
astral77@yonsei.ac.kr



Undergrad. Student Sung Cho
qlcnsksl@yahoo.co.kr



Undergrad. Student Bo Mi Choi
conpoco@hanmail.net



Undergrad. Student Shin Ae Cho
gram26@hanmail.net



Secretary Jin Min Lee
jinmin@alchemy.yonsei.ac.kr

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2000	10	1
	2000	11

2001 2



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B 115

B 116

10,000 counts

37

clean room

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, vacuum line, oven

layout

line

20 °C
3

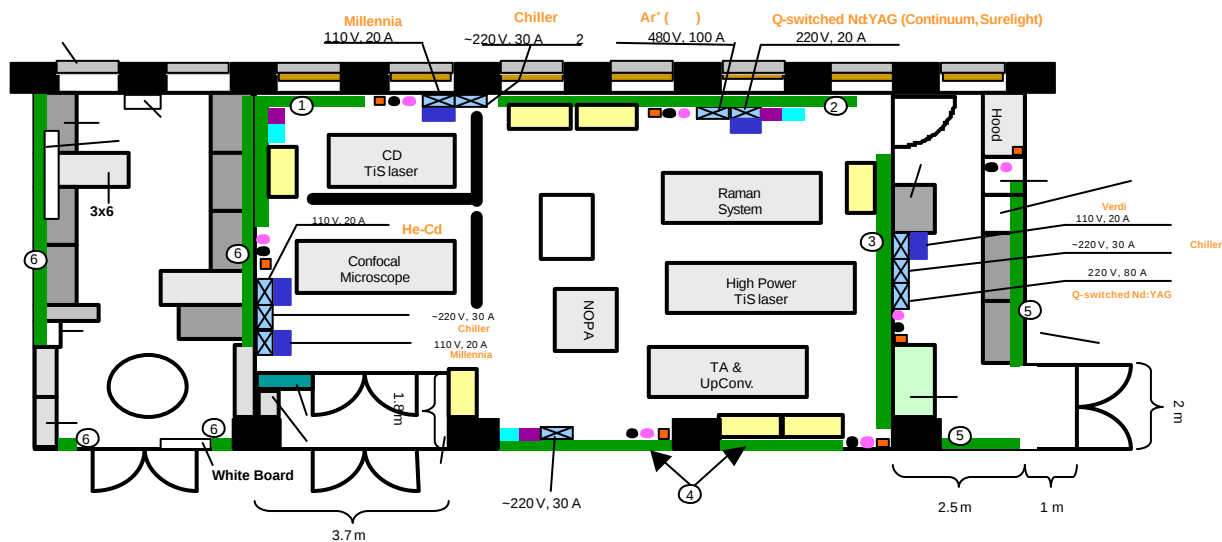
50 %

wet chemistry

, pump, automatic voltage regulator

hood, solvent distillation

cooling water line, line,
7000





1

2000 9 1

" 2000 10 1

porphyrin array resonance Raman normal
mode analysis

()
: porphyrin array resonance
Raman normal mode analysis array



1. 2 1

가 1

. Cavity -dumped Ti:sapphire laser
pulse wavelength tuning range

Noncolinear Optical
Parametric Amplifier (NOPA) 5
fs optical pulse
가 optical components
Confocal microscope He: Cd laser
laser beam spot 0.9 μm

absorption Transient
Optical

Parametric Amplifier pump
independent tunable source
two -color pump/probe IR
Raman

picosecond time-resolved Raman
liquid nitrogen cooled CCD detector
picosecond Raman data

nanosecond cw laser Raman
normal mode
analysis molecular orbital calculation
porphyrin array electronic
structure

◆ Full Paper

1. N. Q. Liem, V. X. Quang, D. X. Thanh, J. I. Lee, A. K. Viswanath and D. Kim, "Biexciton Photoluminescence in cubic ZnS single crystals", *App. Phys. Lett.* **75(25)**, 3974 (2000).

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9. J. -W. Choi, Y. -S. Nam, S. -Y. Oh, D. Kim and W. H. Lee, "Development and Application of a Direct Beam Lithography for the Bioelectronic Device", *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **349**, 295-298 (2000).

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12. Y. H. Kim, H. S. Cho, Dongho Kim, S. K. Kim, N. Yoshida and A. Osuka, "Photophysical Properties of meso, meso-linked Porphyrin Arrays: Steady-state and Time-resolved Fluorescence Polarization", *Syn. Met.* **117**, 183(2001).

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14. Y.-T. Park, C.-H. Jung, M.-S. Kim, and K.-W. Kim, "Photoreaction of 2-Halo-*N*-pyridinylbenzamide: Intramolecular Cyclization Mechanism of Phenyl Radical Assisted with *n*-Complexation of Chlorine Radical", *J. Org. Chem.* **66**(7), 2197(2001).

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Violation of the Kasha's Rule", *J. Phys. Chem. B* in press (2001).

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25. J. -W. Choi, Y. -S. Nam, H. -G. Choi, W. H. Lee, D. Kim, and M. Fujihira, "Rectified Photocurrent of the Protein-Based Bio-Photodiode" *App. Phys. Lett.* in press, 2001.

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3. 가
가

♣ 2001. 4. 15 – 2001.4.18

Professor Atsuhiko Osuka (Department of Chemistry, Kyoto University, Kyoto, Japan)

Osuka 가 Porphyrin Array
steady-state
fused porphyrin arrays
photophysical processes strapped
porphyrin dimer electronic transition origin
Molecular Orbital calculation



♣ 2001. 5. 10

Professor Keiichi Kaneto (Kyushu Institute of Technology, Japan)

Dr. Yasuo Wada (Hitachi Co., Japan)

Molecular Wire Electrical Conductance
Molecular Electronics

♣ 2001. 6. 8.

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