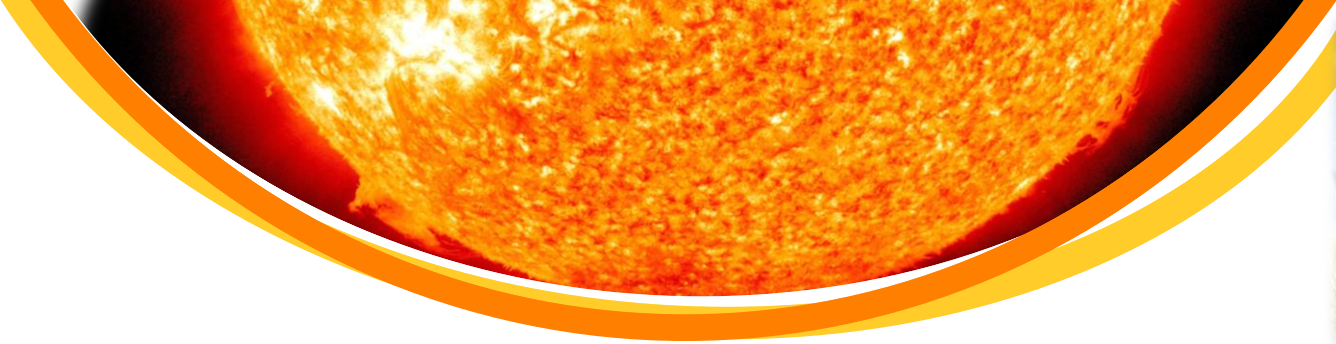
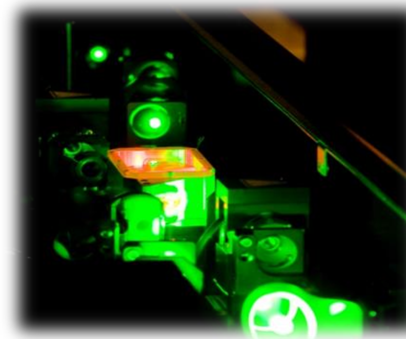


Time-resolved Spectroscopy of Solar Harvesting Complexes



<u>Julie Kho</u>

Ali Hosseini, Peter Boyd, and Cather Simpson

THE UNIVERSITY OF AUCKLAND
FACULTY OF SCIENCE

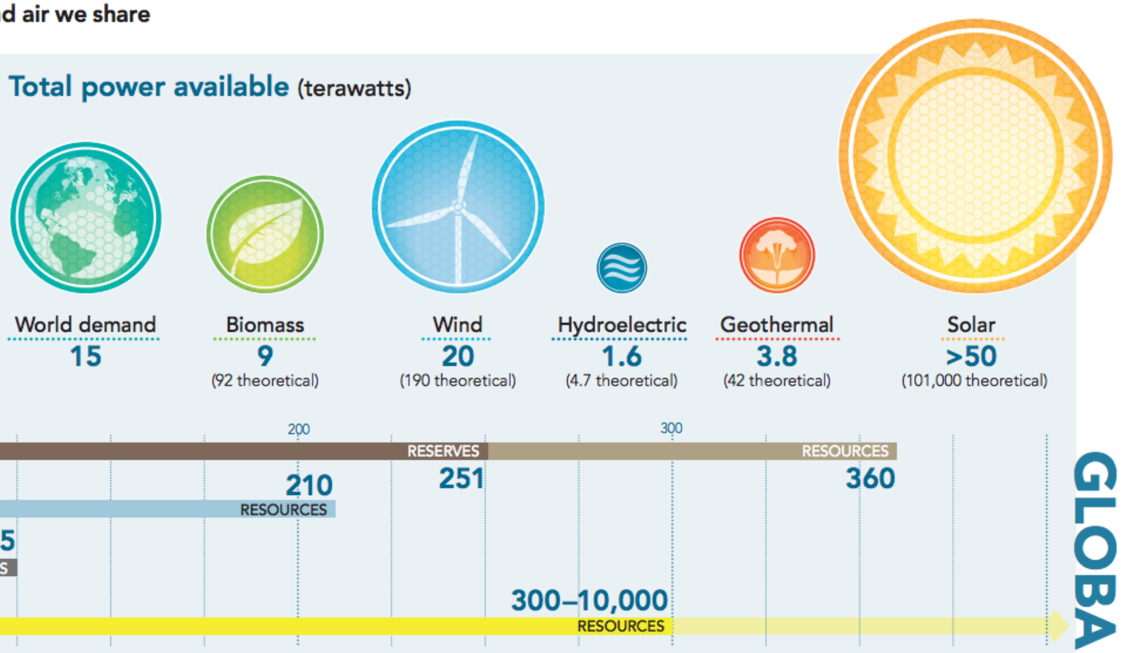
The MacDiarmid Institute
for Advanced Materials and Nanotechnology

Photon Factory

2013 Chemical Sciences Research Showcase

Photon Factory group

The World's Energy Crisis



Energy's Tricky Tradeoffs

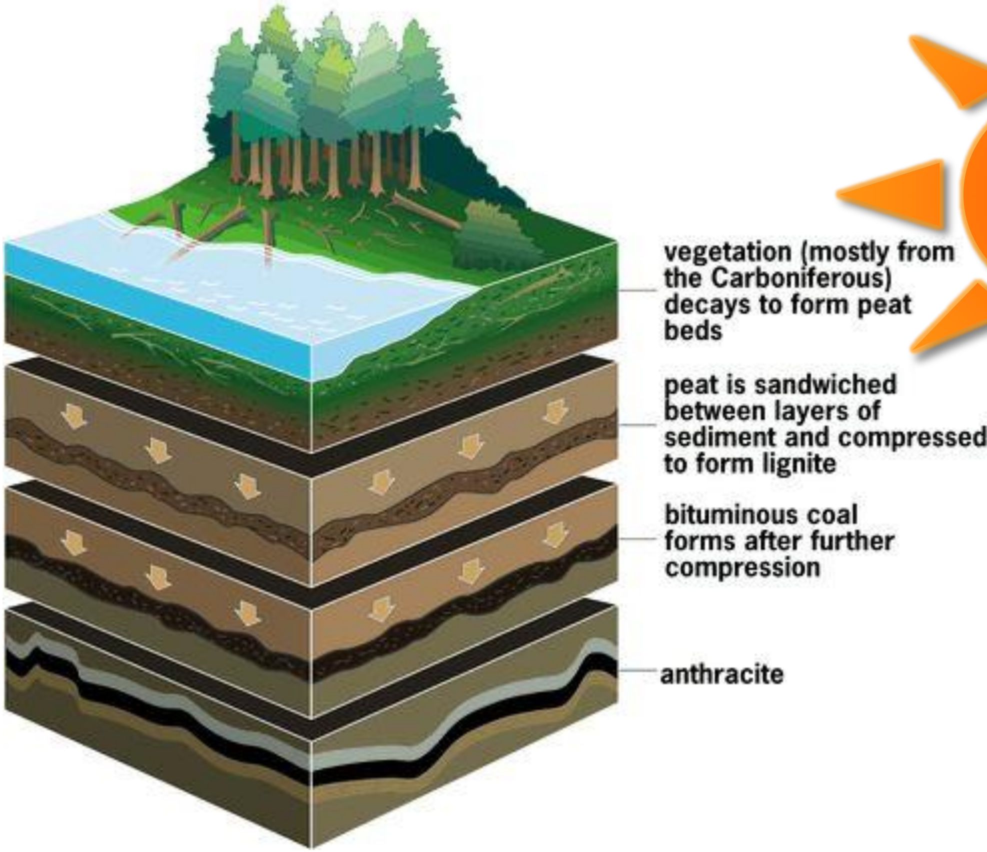
The world's "energy problem" is in fact a slew of technological and sociological challenges involving the use of the land, water, and air we share

I've got sunshine, plenty of sunshine …
Sooner or later, humanity must move away from fossil fuels, finite resources that produce planet-warming greenhouse gases. At first blush, Earth appears to have power to spare. The total power from sunlight striking the ground is a whopping 101,000 terawatts, and experts estimate that we could capture enough of that to exceed by a wide margin the 15 terawatts of power that the world's population now consumes.

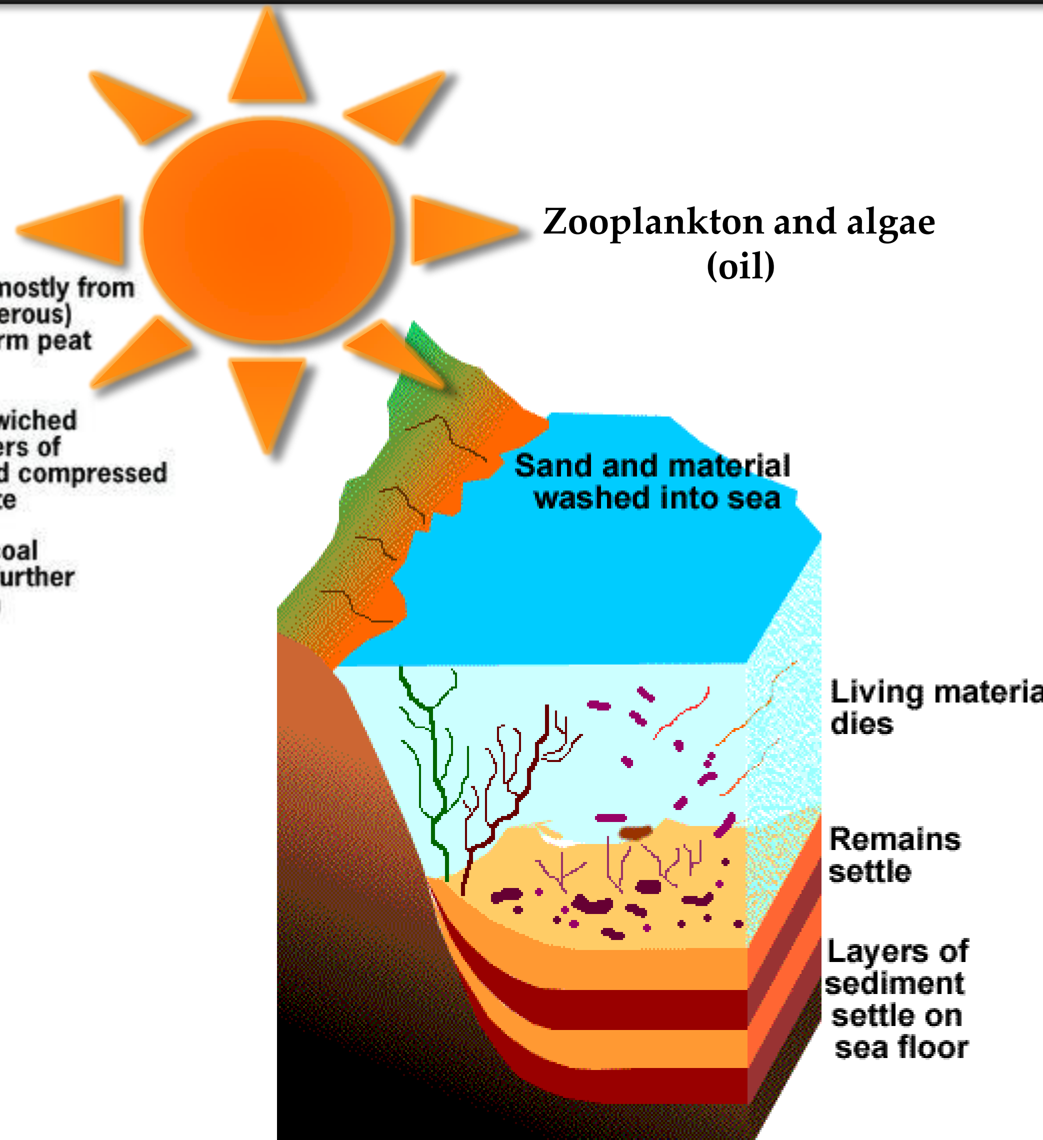
SOURCE: *WORLD ENERGY ASSESSMENT 2000*/UNDP; *WEA 2004*/UNDP; *REPORT OF THE INTL. GEOTHERMAL ASSOCIATION TO THE U.N. COMMISSION ON SUSTAINABLE DEVELOPMENT 2001*; SCLATER *ET AL., JOURNAL OF GEOPHYSICAL RESEARCH* **86** (1981); NASA

13 AUGUST 2010 VOL 329 SCIENCE www.sciencemag.org

Fossil Fuels are Solar Energy



Carboniferous
(coal)

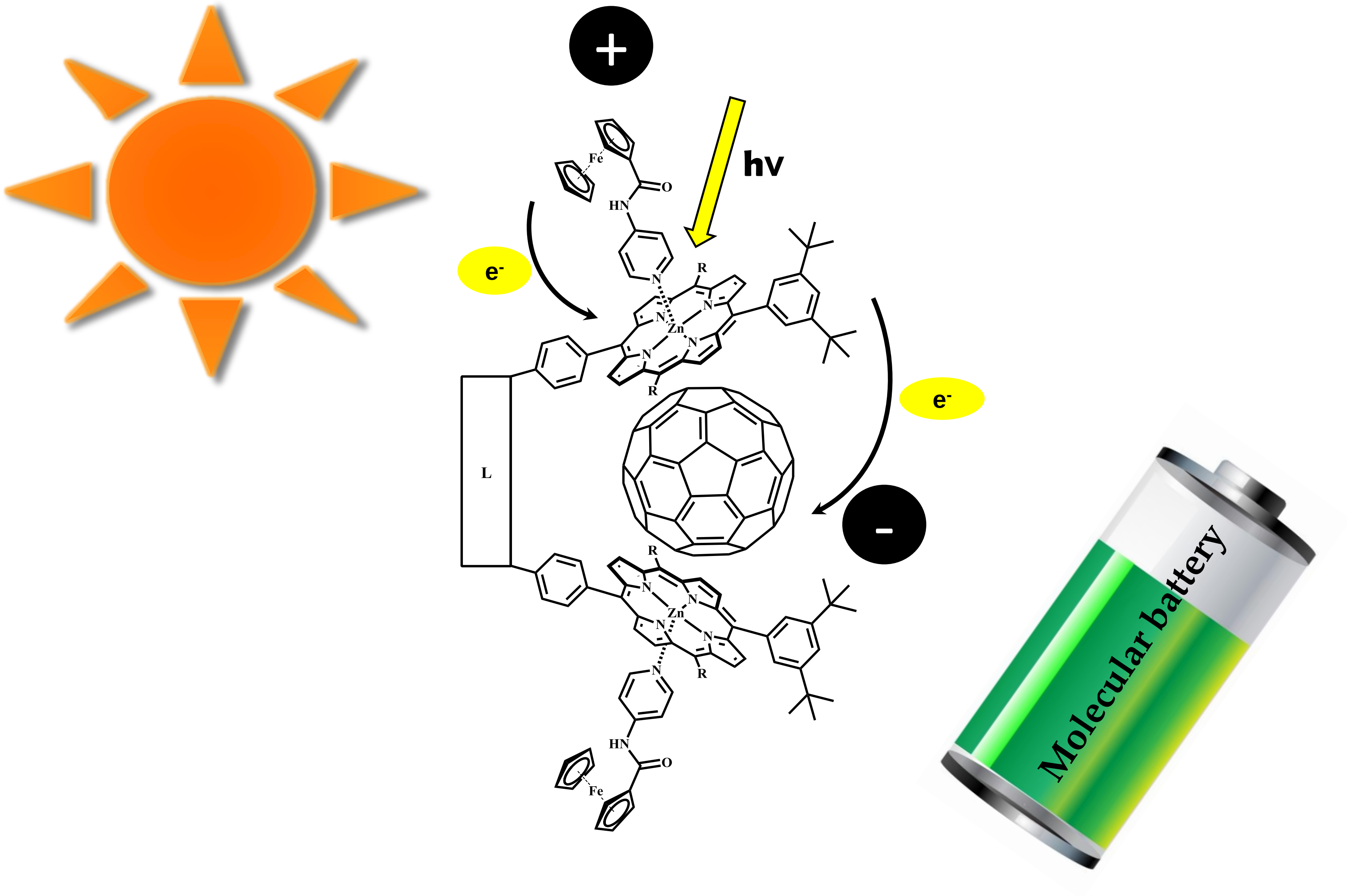


Zooplankton and algae
(oil)

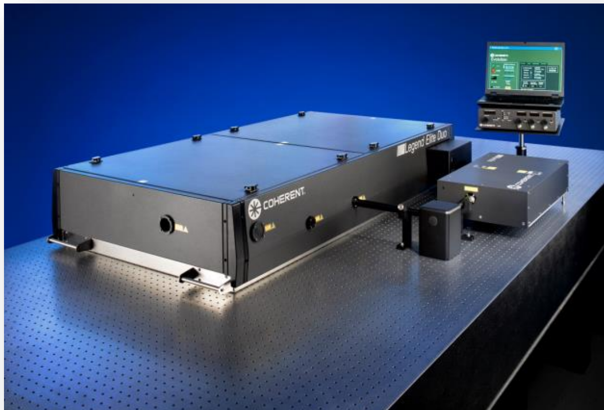
~300-400 million years!

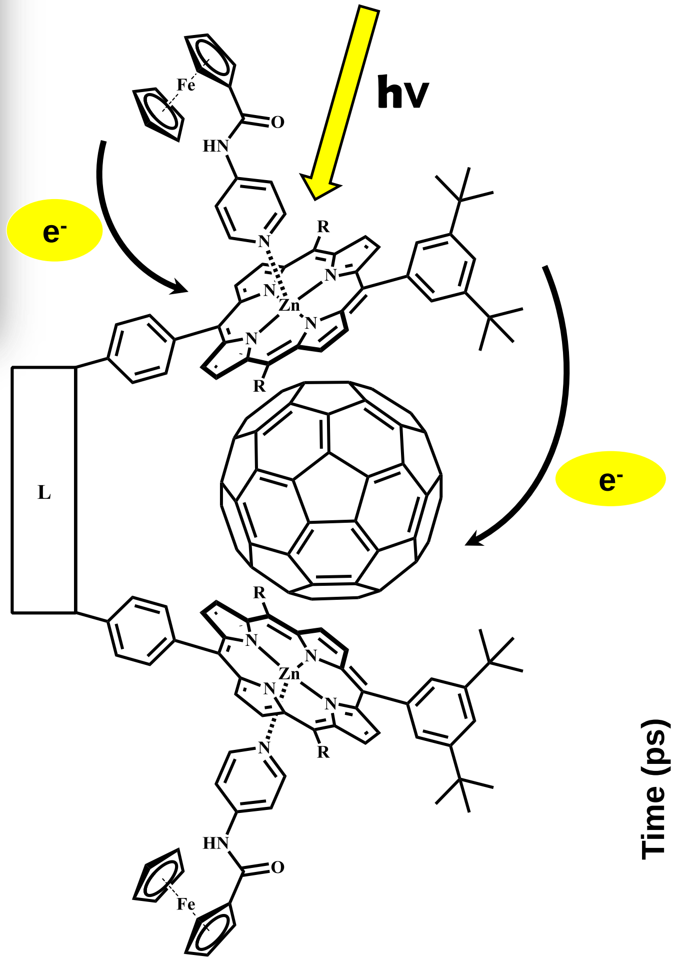
http://media.tiscali.co.uk/images/feeds/hutchinson/ency/0008n102.jpg

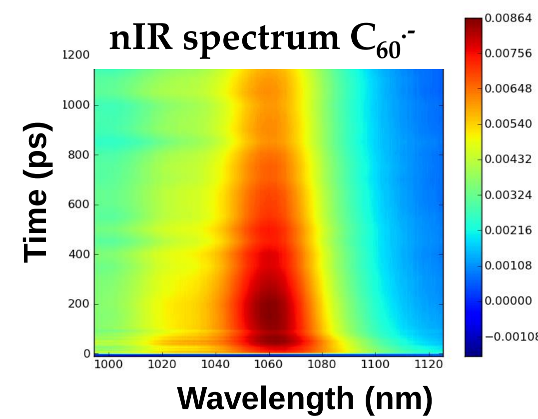
Harvesting Solar Energy



…In a Laser Lab!







Solar Harvesting Complexes

Assoc. Prof. Peter Boyd

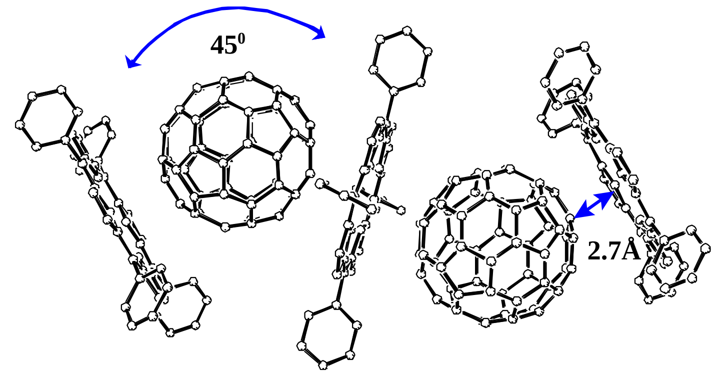
JACS
ARTICLES
Published on Web 05/14/2002

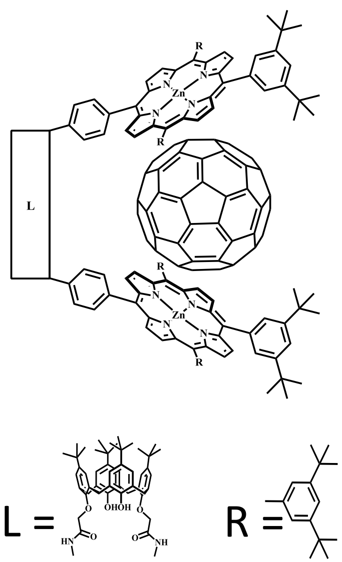
Supramolecular Fullerene-Porphyrin Chemistry. Fullerene Complexation by Metalated “Jaws Porphyrin” Hosts

Dayong Sun,[†] Fook S. Tham,[†] Christopher A. Reed,[*,†] Leila Chaker,[‡] and Peter D. W. Boyd[*,‡]

Contribution from the Departments of Chemistry, University of California, Riverside, California 92521-0403, and The University of Auckland, Private Bag, Auckland, New Zealand

Received November 15, 2001





Dr. Ali Hosseini

JACS
ARTICLES
Published on Web 11/15/2006

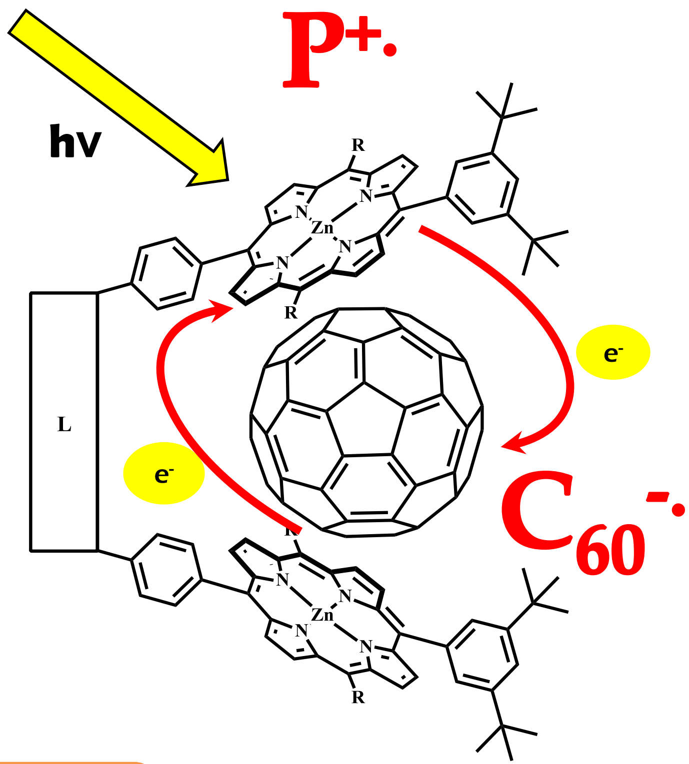
Calix[4]arene-Linked Bisporphyrin Hosts for Fullerenes: Binding Strength, Solvation Effects, and Porphyrin−Fullerene Charge Transfer Bands

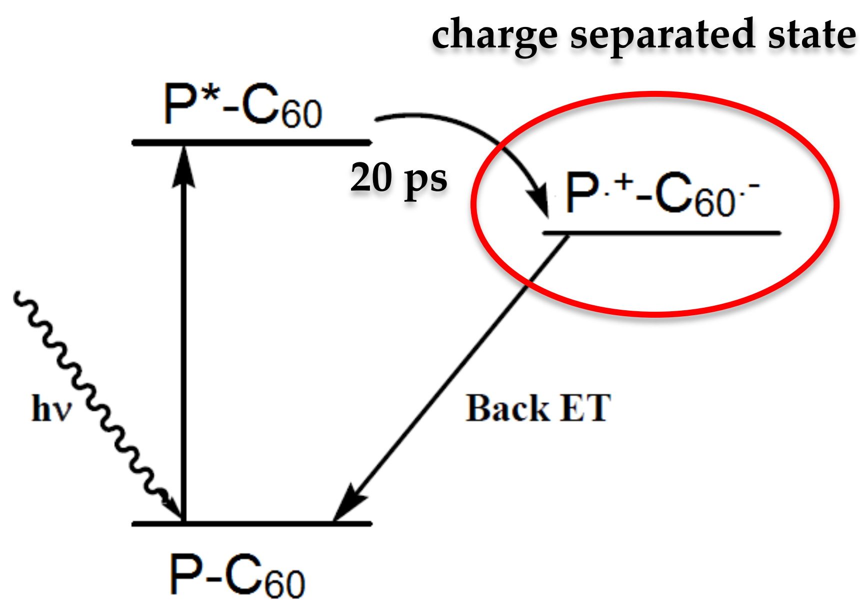
Ali Hosseini,[†] Steven Taylor,[†] Gianluca Accorsi,[‡] Nicola Armaroli,[*,‡] Christopher A. Reed,[*,§] and Peter D. W. Boyd[*,†]

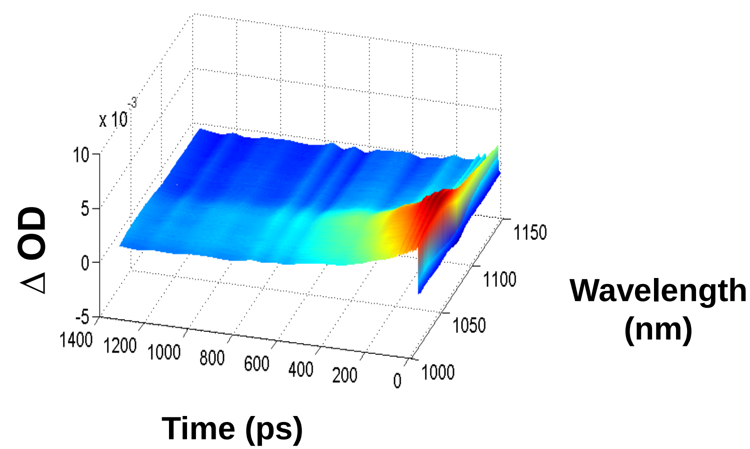
Contribution from the Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand, Molecular Photoscience Group, Istituto per la Sintesi Organica e la Fotoreattività (ISOF), Consiglio Nazionale delle Ricerche (CNR), Via Gobetti 101, 40129 Bologna, Italy, and Department of Chemistry, University of California, Riverside, California 92521

Received August 18, 2006; E-mail: chris.reed@ucr.edu; pdw.boyd@auckland.ac.nz; armaroli@isof.cnr.it

Solar Harvesting Complexes







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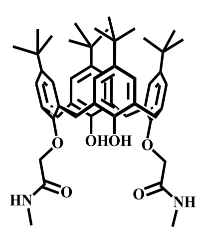
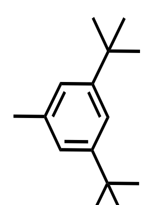
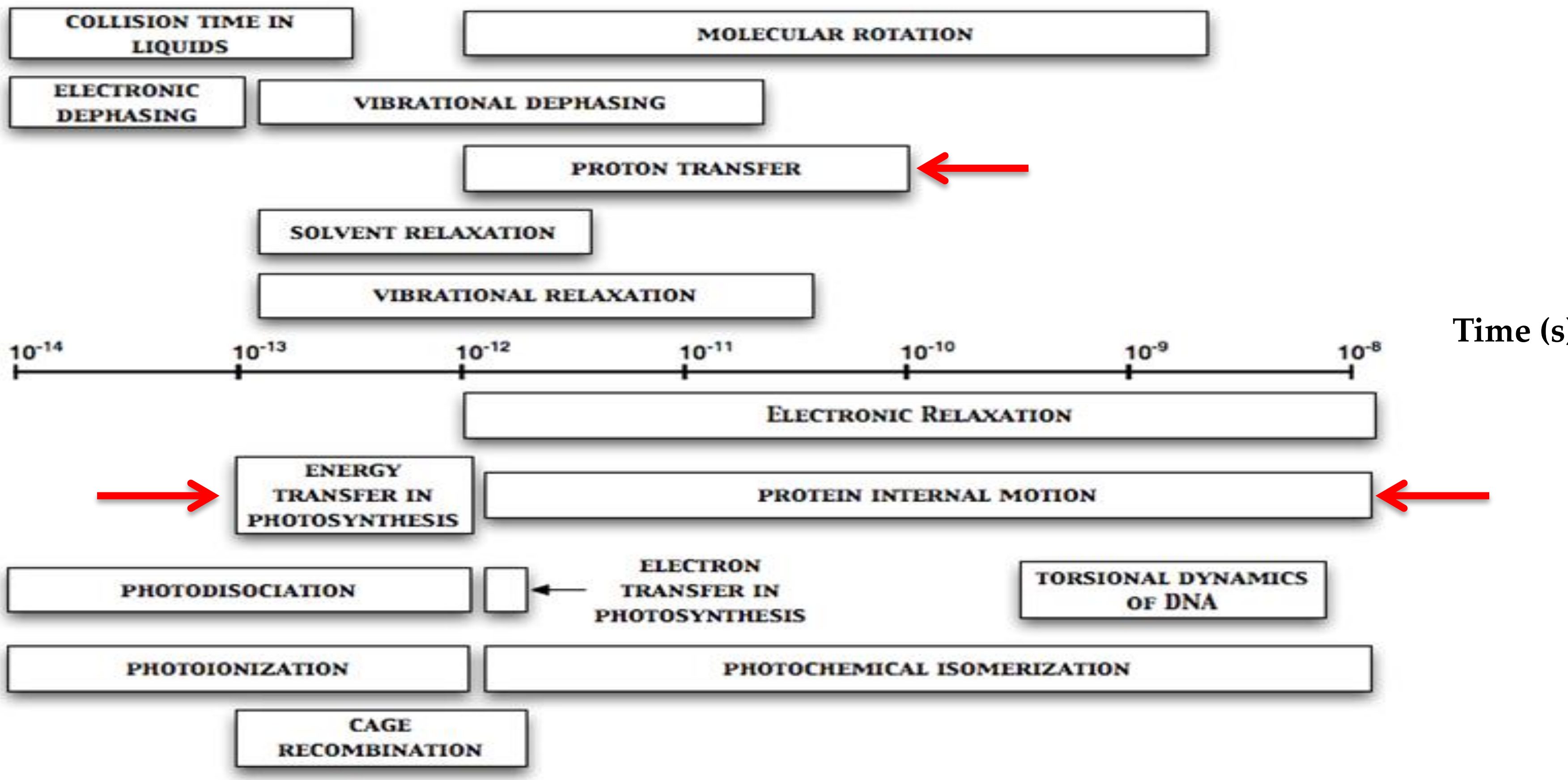
L = 

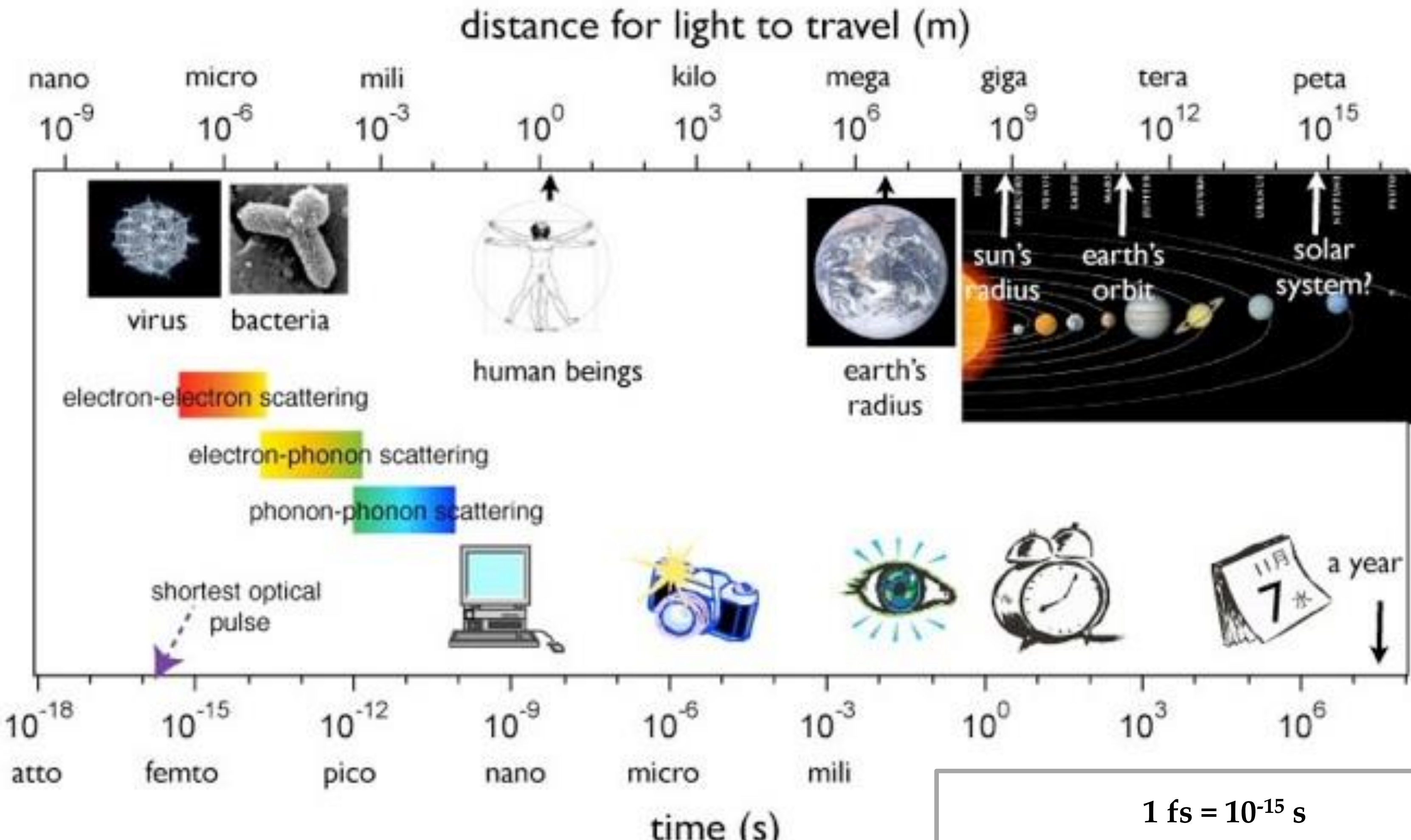
R = 

How long is long-lived?



In photosynthesis, the first charge separation occurs in 3 ps!

How long is long-lived?



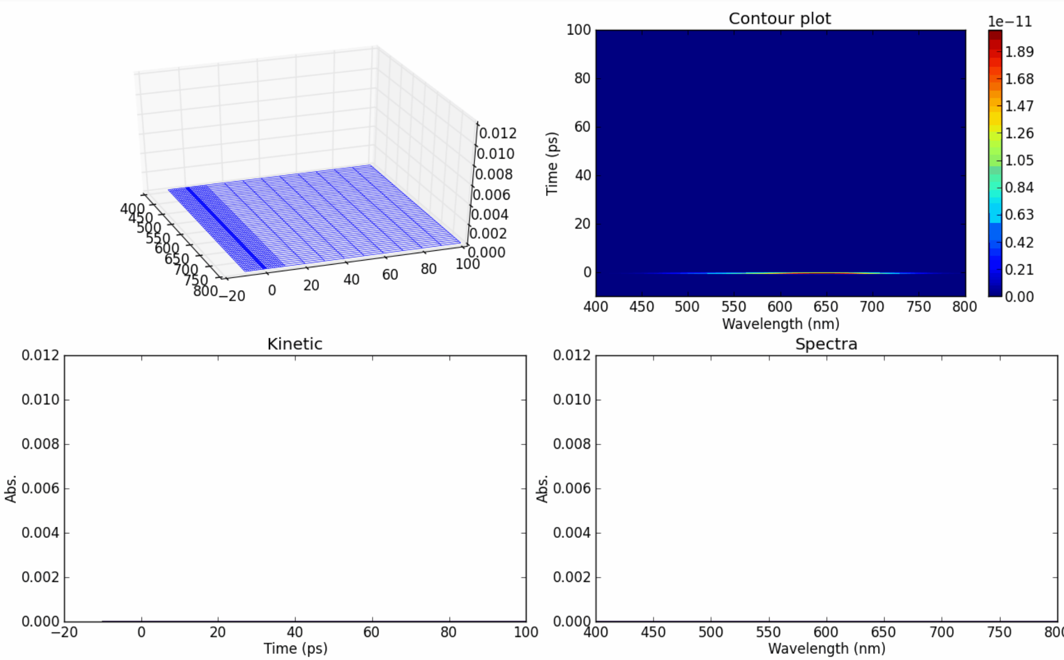
1 fs = 10^{-15} s

1 fs ~ 0.3 'light micrometers'

The size of a virus!

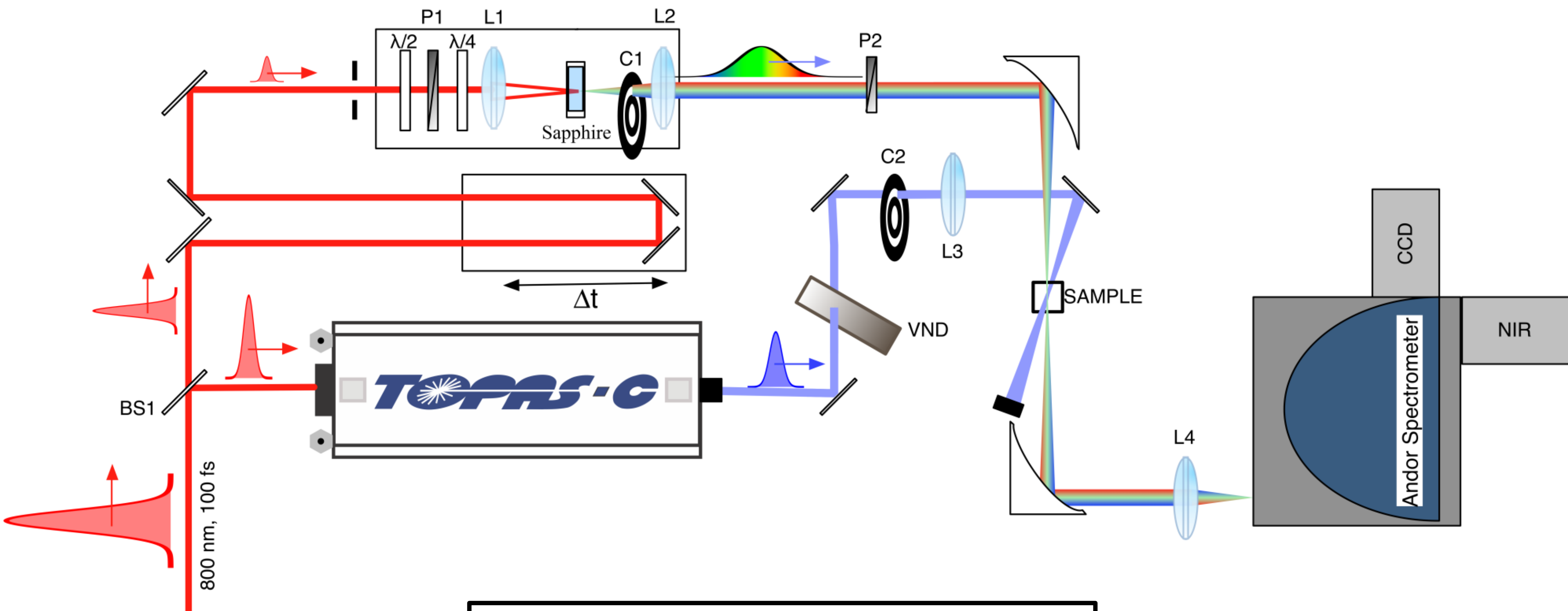
http://www.nims.go.jp/ldynamics/en/How_short.html

Transient Absorption (TrA) Spectroscopy



1. Molecules are excited by a pump laser at a specific wavelength
2. A broadband (white-light) laser overlaps the pump at the sample to measure absorbance at different time delays
3. Change in absorbance data is collected

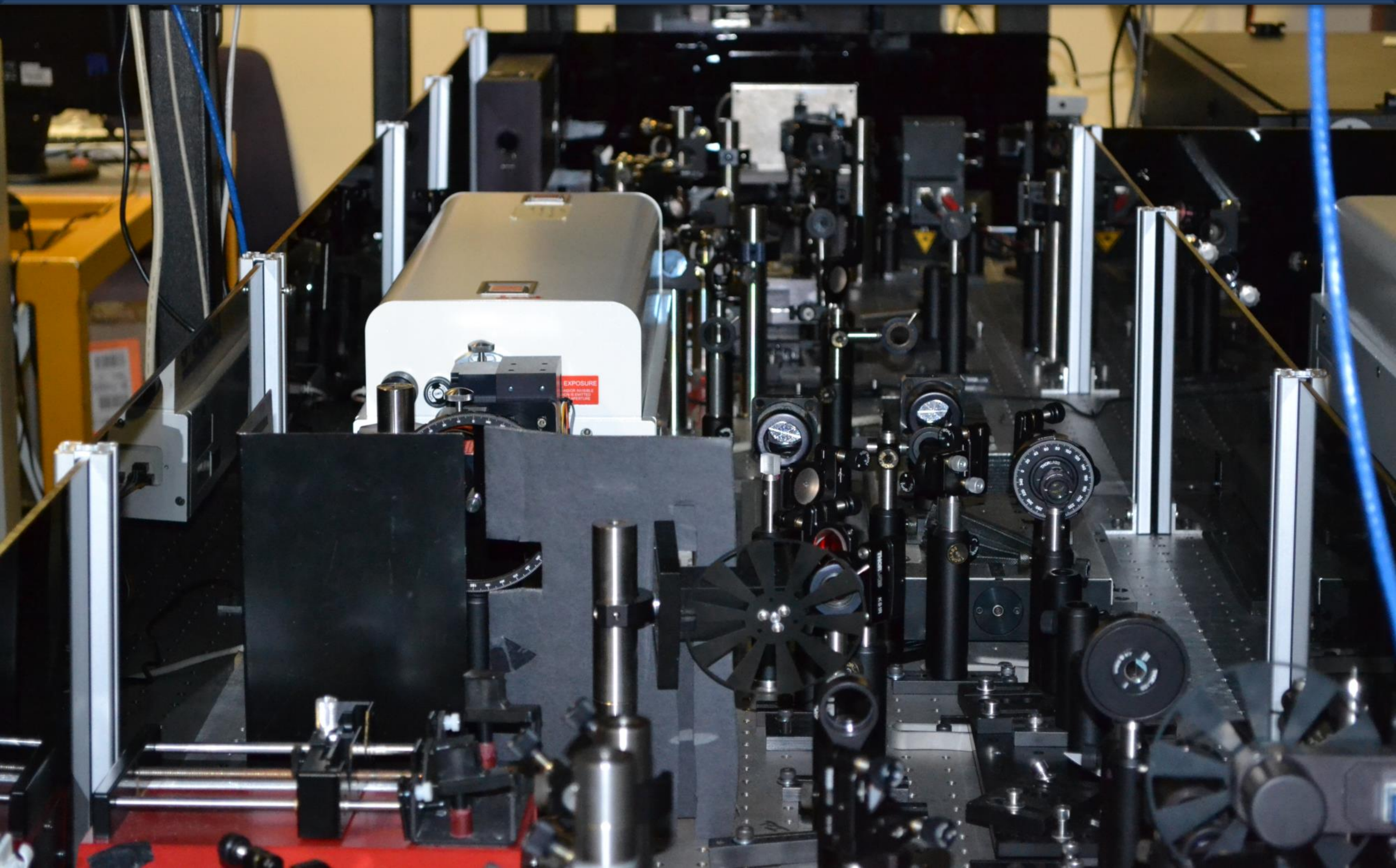
FsTrA Spectroscopy system in The Photon Factory



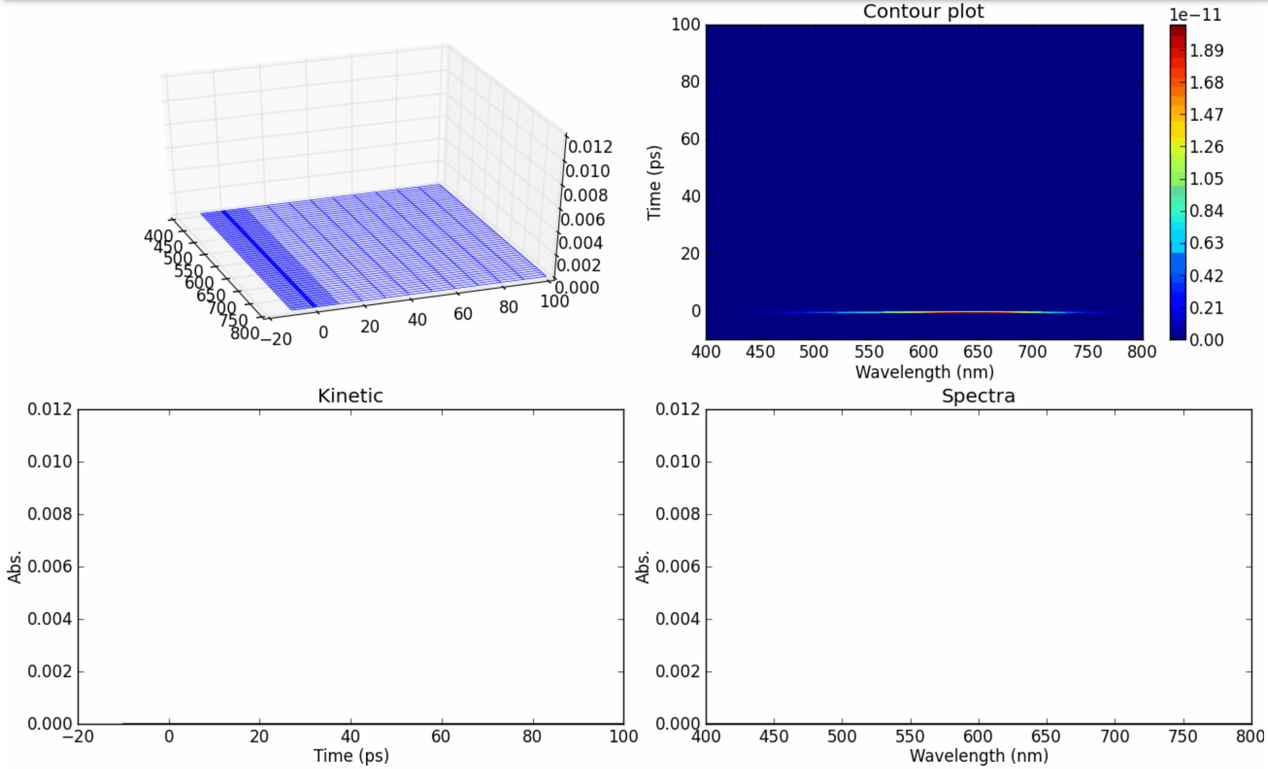
Tunable pump laser: 300-3000 nm
Supercontinuum probe: 430-1500 nm
Delay stage time range: up to 4 ns

Detection cameras
Andor iDus CCD 1024 x 127 active pixels
Andor InGaAs 512 x 1 active pixels

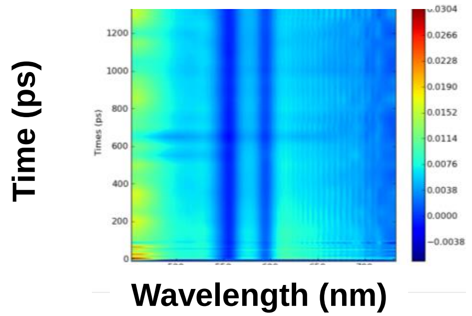
FsTrA Spectroscopy system in The Photon Factory

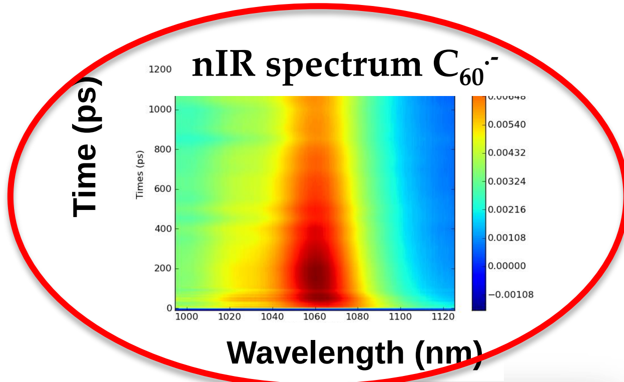


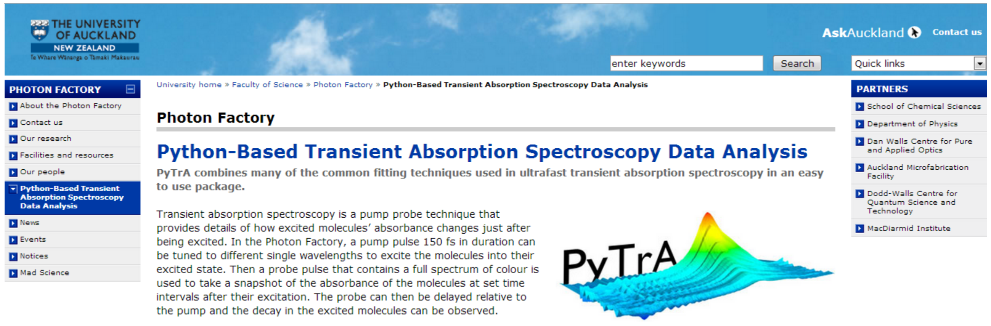
FsTrA Data Analysis



UV-Vis spectrum P•+







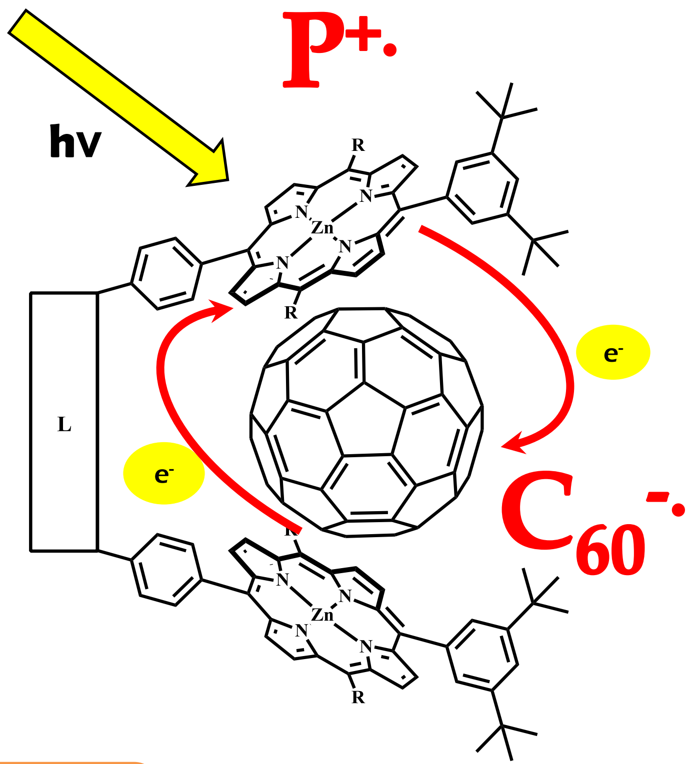
http://www.photonfactory.auckland.ac.nz/uoa/home/photon-factory/pytra

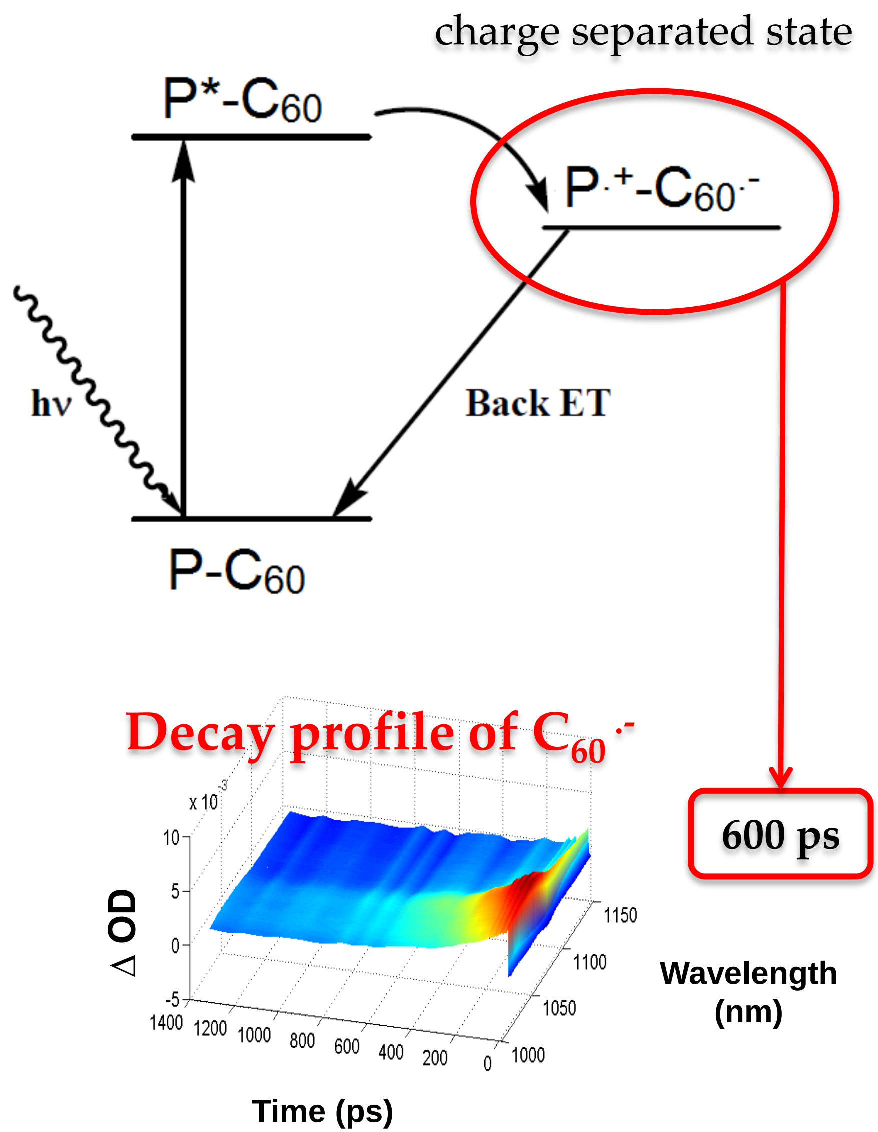
PyTrA 1.0 features:

- Data processing
- Visualization
- Soft modelling
- Hard modelling

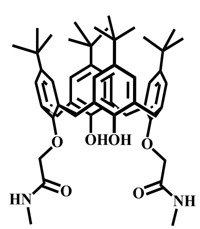
Jake Martin

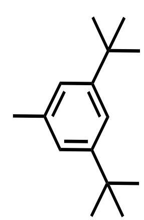
Solar Harvesting Complexes





Dyad

L = 

R = 

Solar Harvesting Complexes

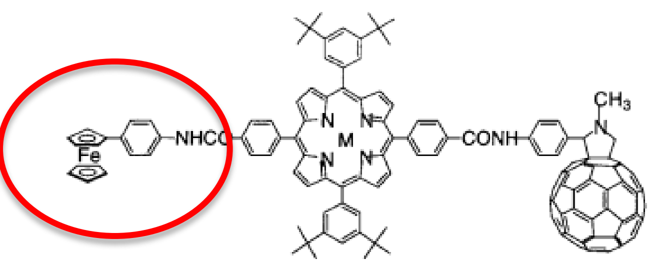
J. Am. Chem. Soc. **2001**, *123*, 2607−2617

Modulating Charge Separation and Charge Recombination Dynamics in Porphyrin−Fullerene Linked Dyads and Triads: Marcus-Normal versus Inverted Region

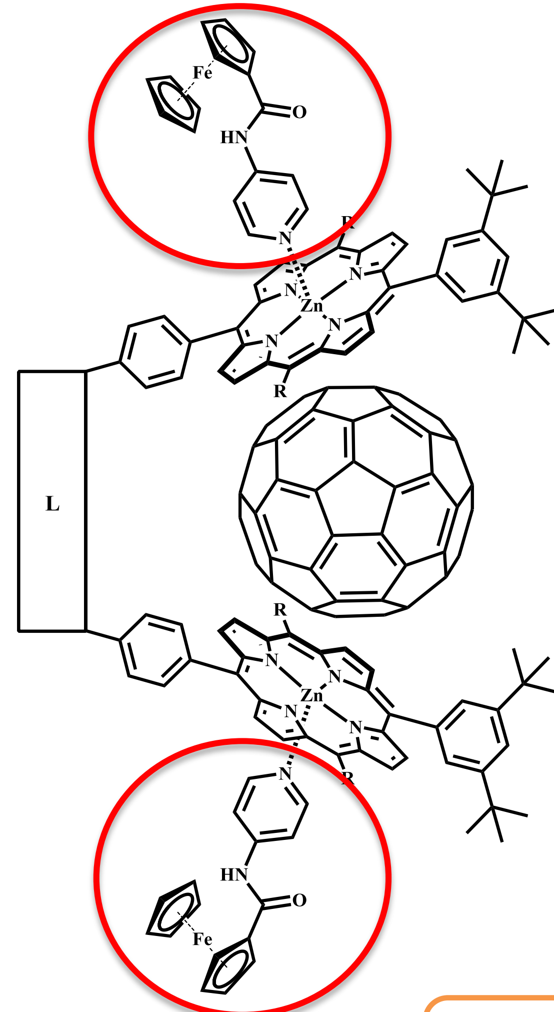
Hiroshi Imahori,*[⊥] Koichi Tamaki,[‡] Dirk M. Guldi,*[,†] Chuping Luo,[†] Mamoru Fujitsuka,[§] Osamu Ito,*[,§] Yoshiteru Sakata,[‡] and Shunichi Fukuzumi*[,⊥]

Contribution from the Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Japan Science and Technology Corporation, Suita, Osaka 565-0871, Japan, The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihoga-oka, Ibaraki, Osaka 567-0047, Japan, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan

Received September 11, 2000. Revised Manuscript Received January 2, 2001



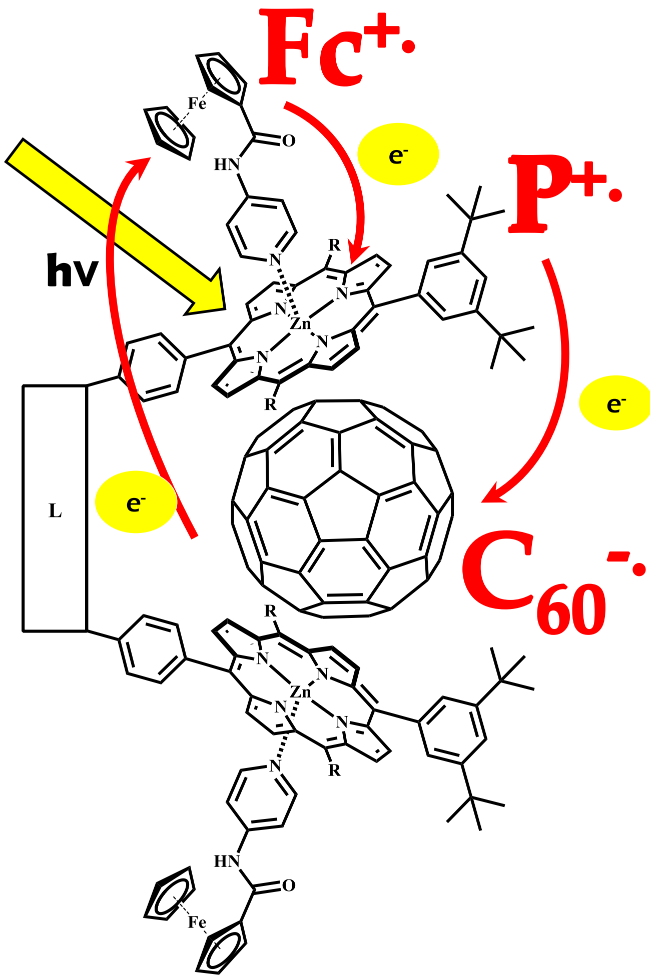
Fc-ZnP-C_{60} (M=Zn)
Fc-H_2P-C_{60} (M=H_2)

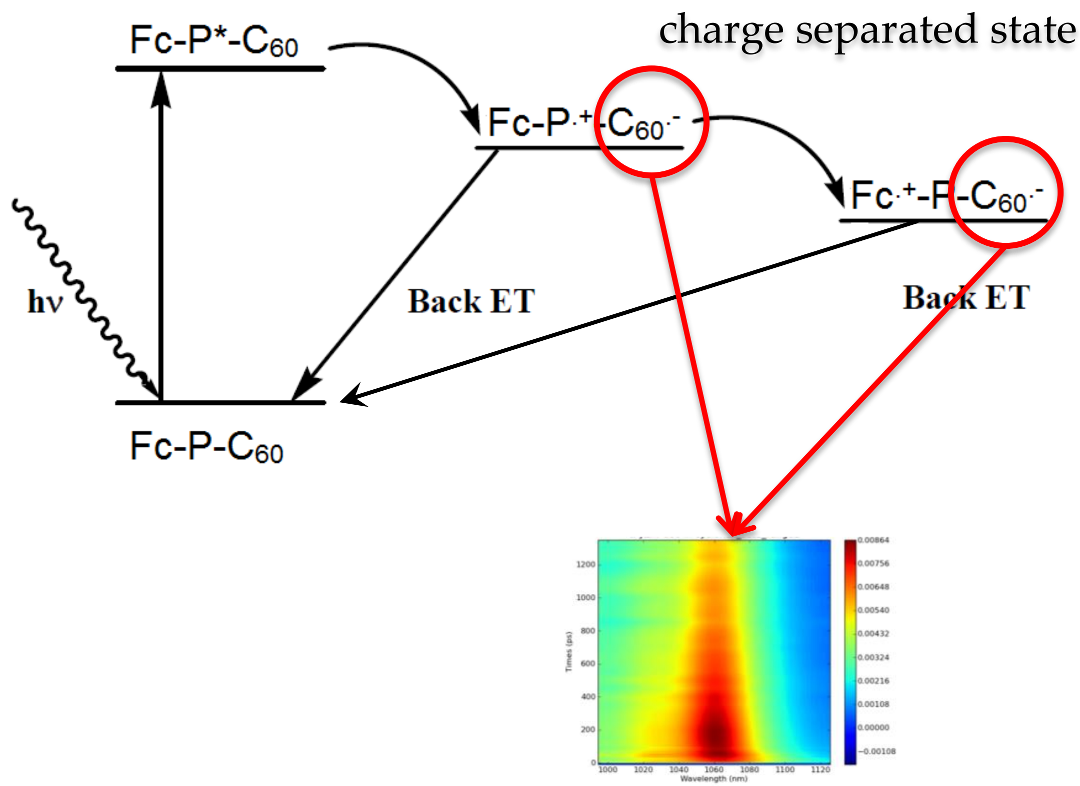


Lifetime of charge separated state of up to 16 μs

Triad

Solar Harvesting Complexes





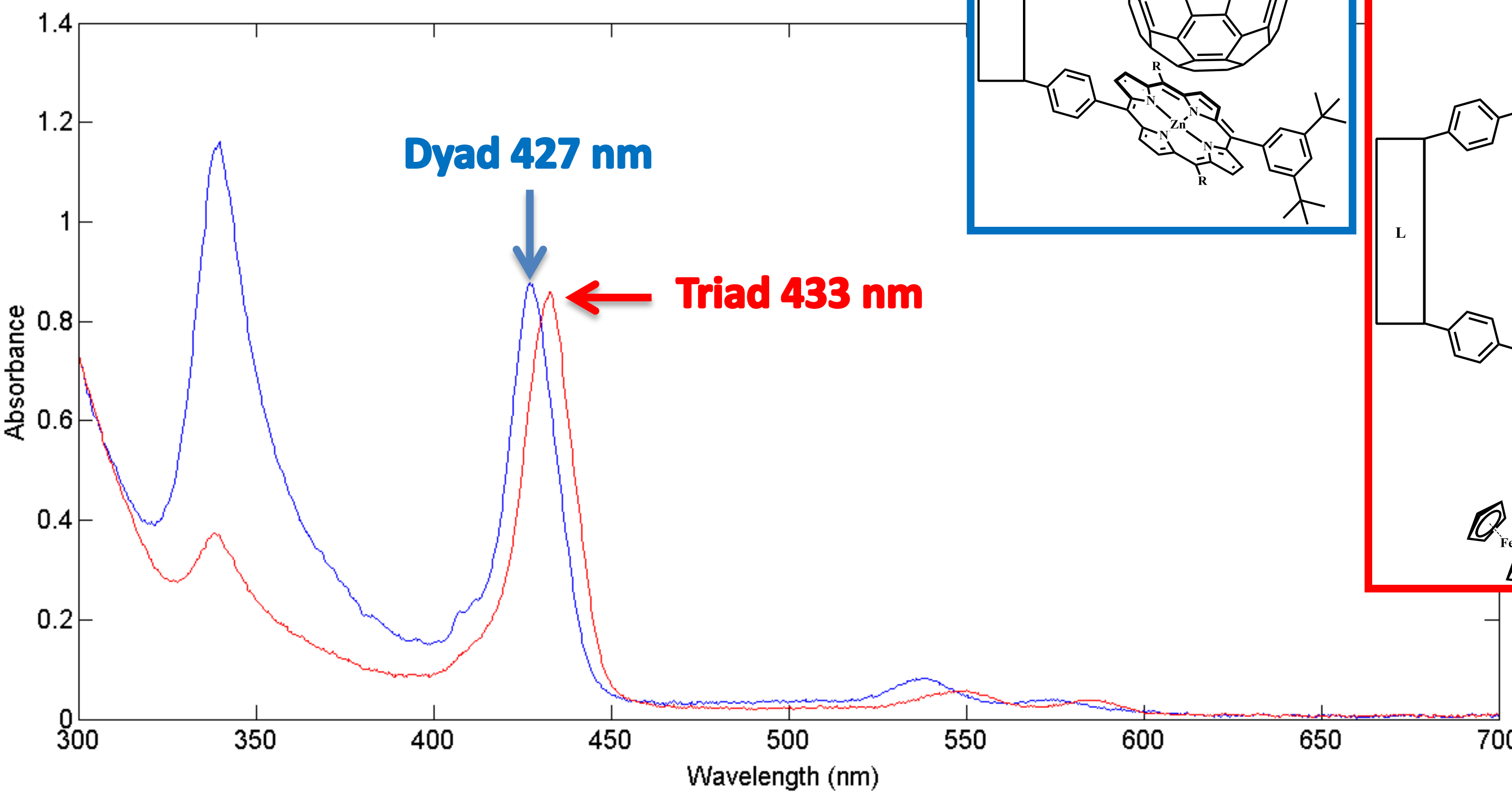
Triad

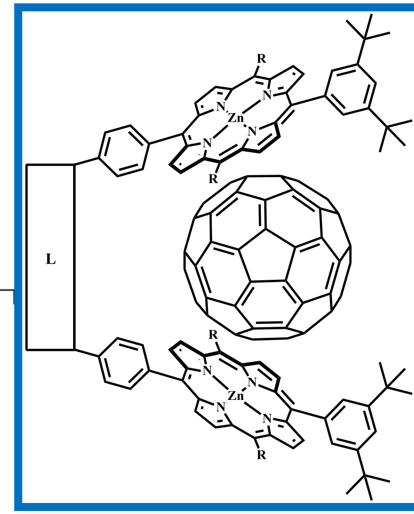
Hypothesis: Triad should have a longer lifetime for the charge separated state

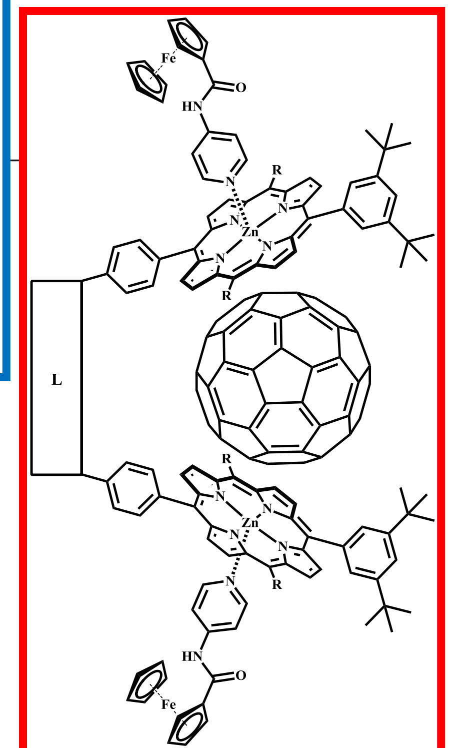
FsTrA Results

Experiment parameters:

Sample OD= 0.8 @ λ_{max}
Pump power = 1 μJ/pulse
Pump wavelength = porphyrin Soret peak (427nm, 433nm)
Probe = 950 – 1120 nm



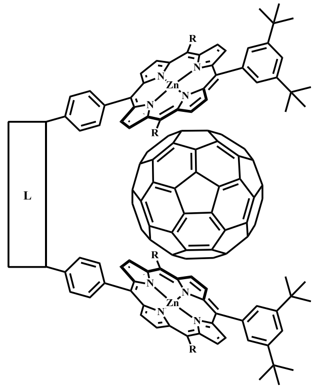




Hypothesis: charge separated state lives longer in triad than in dyad

$C_{60}^{\cdot -}$ lifetime

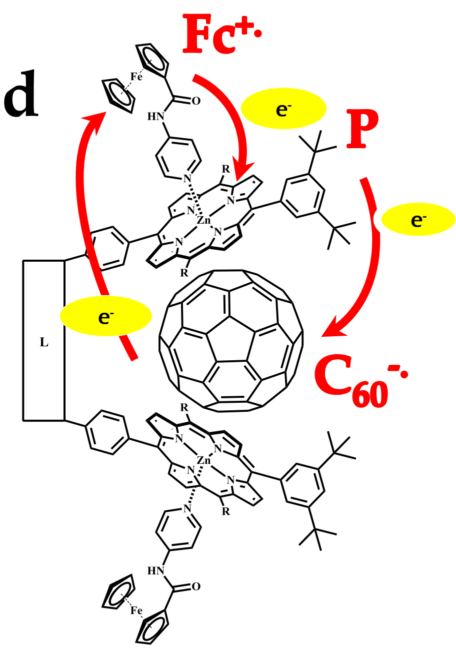
Dyad



	$C_{60}^{\cdot -}$ lifetime
toluene	600 ± 3 ps
cyclohexane	440 ± 2 ps

Grimm B, *et al.* (2011) *Chemical Science* 2(8):1530-1537.

Triad

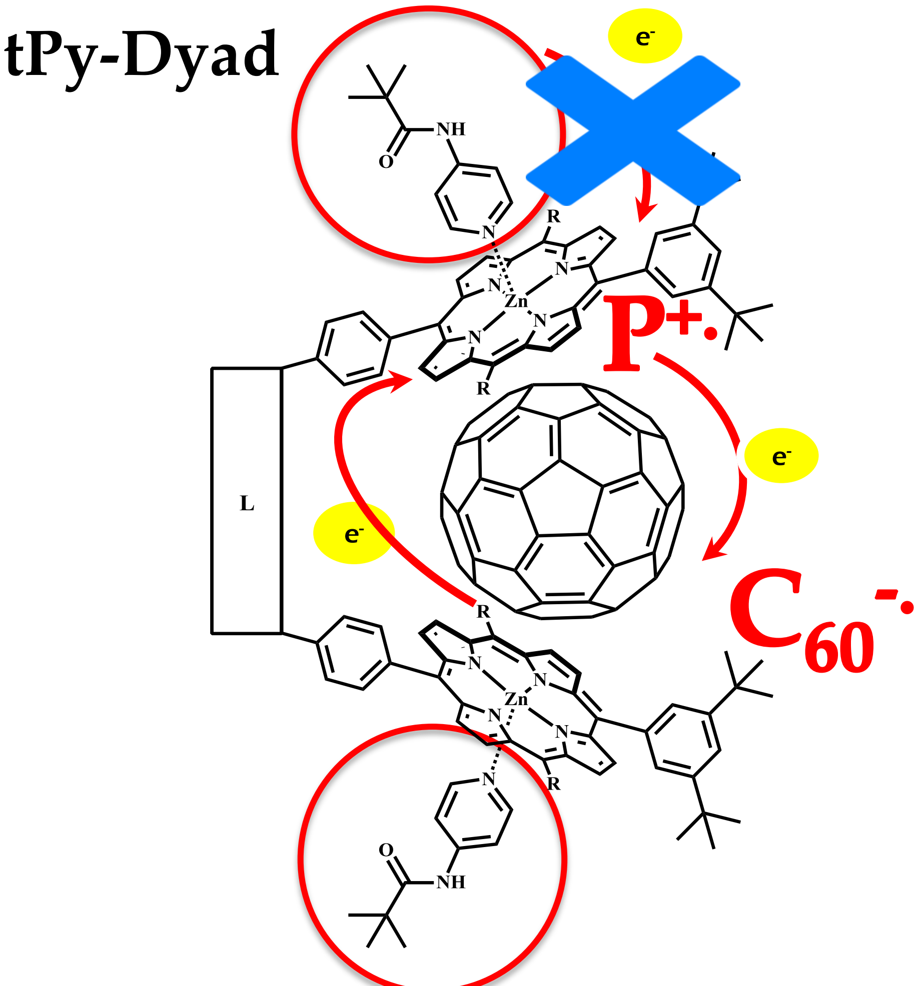


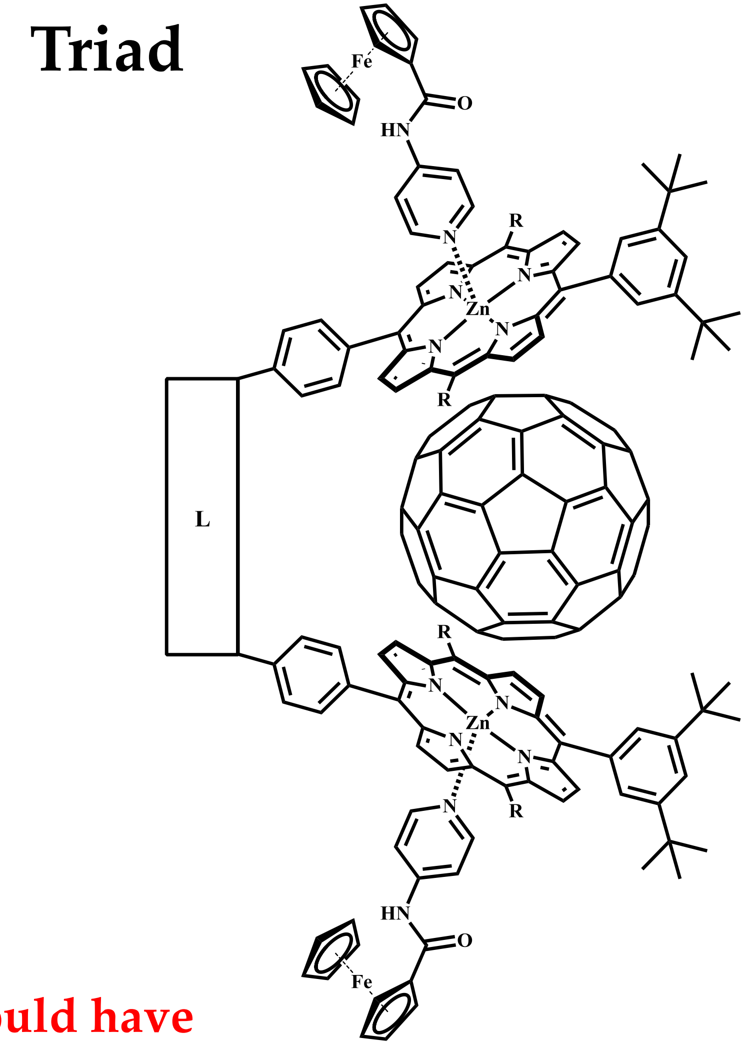
	$C_{60}^{\cdot -}$ lifetime
toluene	1180 ± 18 ps
cyclohexane	1220 ± 11 ps

Consistent with our hypothesis !

But…the molecule degraded in the beam

Is it electron transfer?



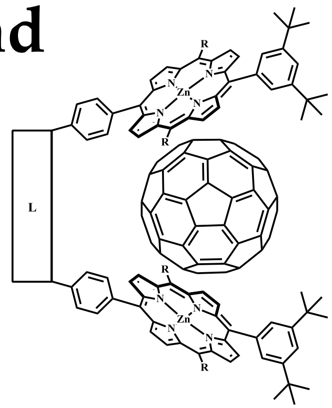


No secondary donor, should have same ET rate as the other dyad

It's the ligation, not the electron transfer

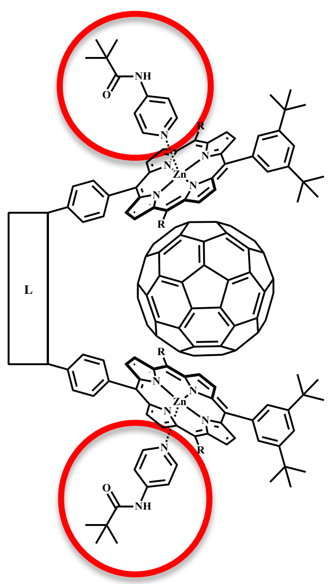
$C_{60}^{\cdot -}$ lifetime

Dyad



	$C_{60}^{\cdot -}$ lifetime
toluene	600 ± 3 ps
cyclohexane	440 ± 2 ps

tPy-Dyad



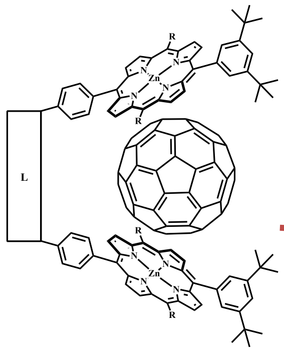
	$C_{60}^{\cdot -}$ lifetime
toluene	1660 ± 20 ps
cyclohexane	2420 ± 10 ps

This complex degraded too!

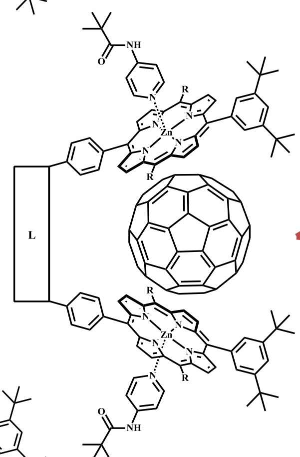
the coordination of pyridine moiety to Zn bis-porphyrin results in the lifetime changes

Lifetime Measurements Summary

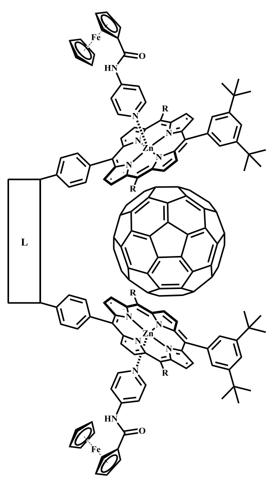
Dyad



tPy-Dyad



Triad

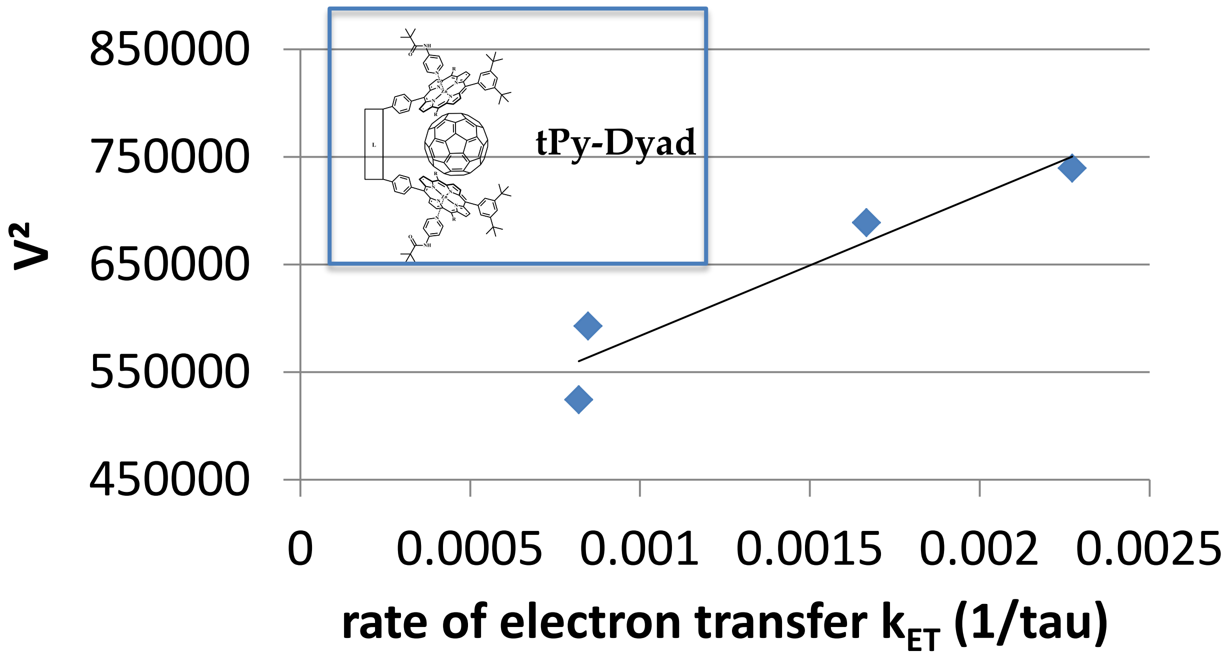


	Solvent	$C_{60}^{\cdot -}$ lifetime	
Dyad	toluene	600 ± 3 ps	830 cm^{-1}
Dyad	cyclohexane	440 ± 2 ps	860 cm^{-1}
tPy-Dyad	toluene	1660 ± 20 ps	
tPy-Dyad	cyclohexane	2420 ± 10 ps	
Triad	toluene	1180 ± 18 ps	770 cm^{-1}
Triad	cyclohexane	1220 ± 11 ps	724 cm^{-1}

$$V = \frac{2.06 \times 10^{-2} \left(\varepsilon_{\max} \nu_{\max} \Delta \nu_{1/2} \right)^{1/2}}{R_{cc}}$$

V = electronic coupling (in cm^{-1})
e_{max} = extension coefficient of CT band (in $mol^{-1}cm^{-1}$)
n_{max} = frequency of CT band (in cm^{-1})
Dn_{max} = full width at half height (in cm^{-1})
R_{cc} = porphyrin centre to fullerene centre distance = 6.25 Å

Correlation between $C_{60}^{\cdot -}$ lifetime and V



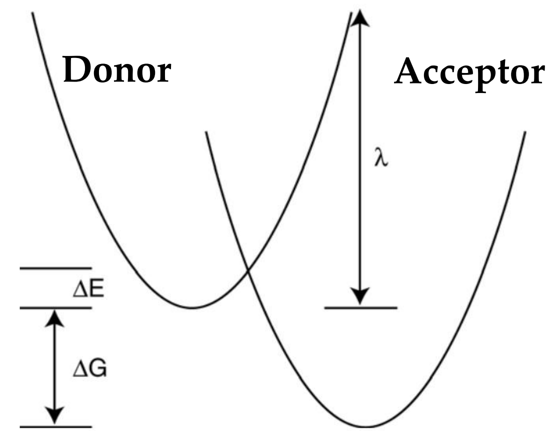
V = electronic coupling (in cm^{-1})

$$V = \frac{2.06\times10^{-2}\left(\varepsilon_{max}\nu_{max}\Delta\nu_{1/2}\right)^{1/2}}{R_{cc}}$$

V = electronic coupling (in cm^{-1})
e_{max} = extension coefficient of CT band (in $mol^{-1}cm^{-1}$)
n_{max} = frequency of CT band (in cm^{-1})
Dn_{max} = full width at half height (in cm^{-1})
R_{cc} = porphyrin centre to fullerene centre distance = 6.25 Å

- ➢ Approximation from charge transfer bands

Marcus theory of electron transfer

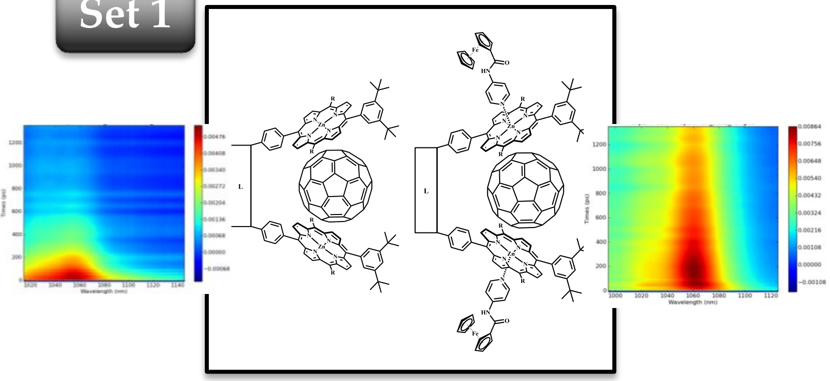


$$k_{ET} = \left(\frac{4\pi^3}{h^2\lambda k_B T}\right)^{1/2} V^2 \exp\left[-\frac{(\Delta G^0{}_{ET}+\lambda)^2}{4\lambda k_B T}\right]$$

V = electronic coupling (in cm^{-1})
k_B = Boltzmann constant
h = Planck constant
T = absolute temperature
ΔG^0 = free energy change
λ = reorganization energy

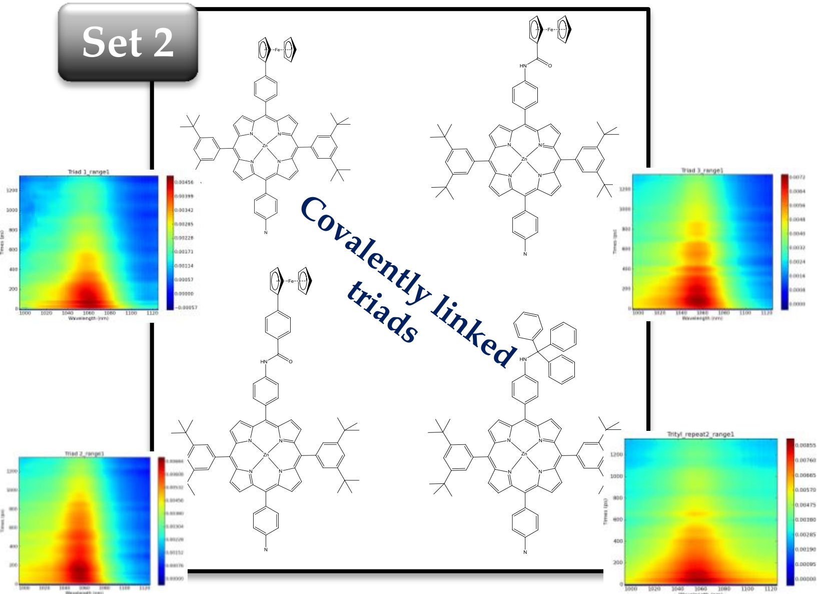
What's next?

Set 1

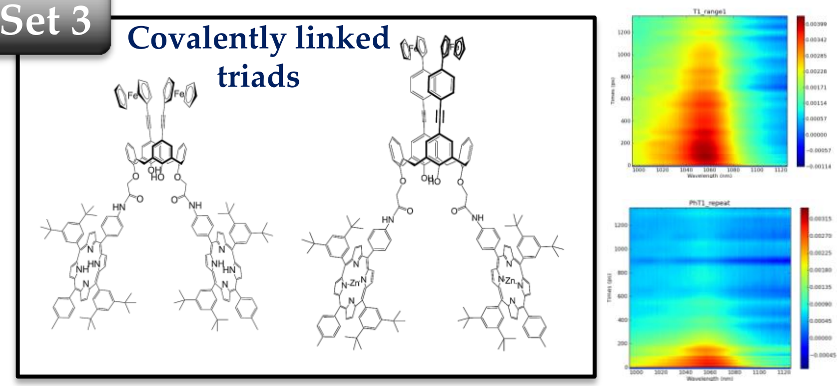


- Test the electronic coupling constant idea further
- Measure $P^{+\cdot}$ decay in UV-VIS

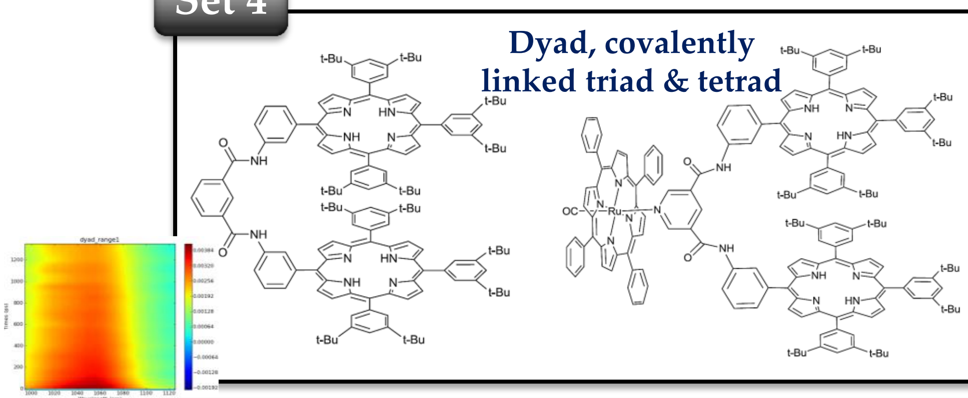
Set 2



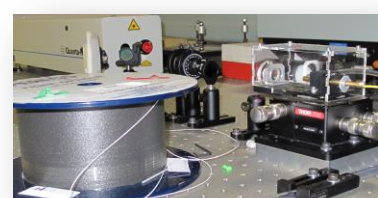
Set 3



Set 4



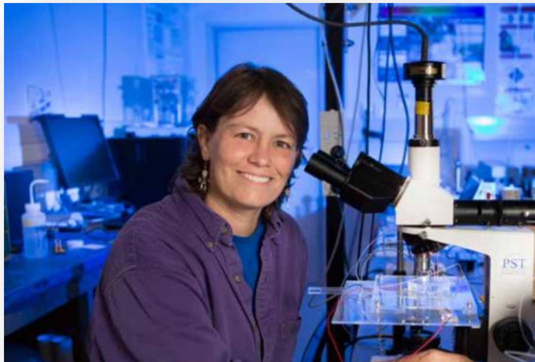
Nanosecond TrA Spectroscopy System



Longer lifetime measurements (ns-ms)

Julie L.H. Kho, Optics Communications, Volume 294, 1 May 2013, Pages 250-254.

Acknowledgements



Assoc. Prof. Cather Simpson
Director of Photon Factory

Assoc. Prof. Peter Boyd

Dr. Ali Hosseini

Dr. Charles Rohde

Thank you for your attention!

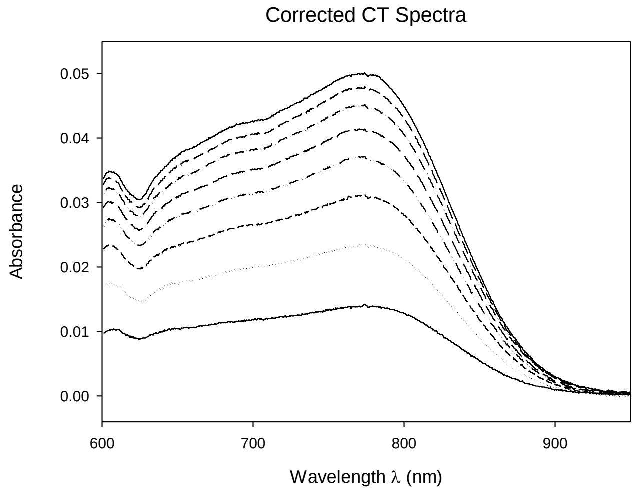
Sarah Thompson

Jake Martin

THE UNIVERSITY OF AUCKLAND
FACULTY OF SCIENCE

The MacDiarmid Institute
for Advanced Materials and Nanotechnology

Photon Factory



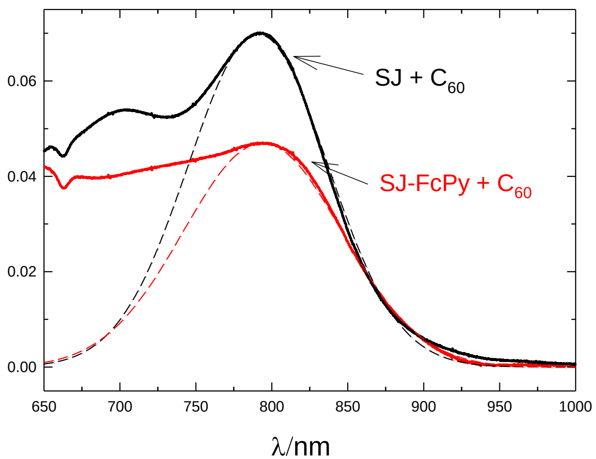
$$V = \frac{2.06 \times 10^{-2} \left(\varepsilon_{max} \nu_{max} \Delta \nu_{1/2} \right)^{1/2}}{R_{cc}}$$

Where

V = electronic coupling (in cm^{-1})
ε_{max} = extension coefficient of CT band (in $mol^{-1}cm^{-1}$)
ν_{max} = frequency of CT band (in cm^{-1})
$\Delta\nu_{max}$ = full width at half height (in cm^{-1})
R_{cc} = porphyrin centre to fullerene cntre distance = 6.25 Å

Cyclohexane

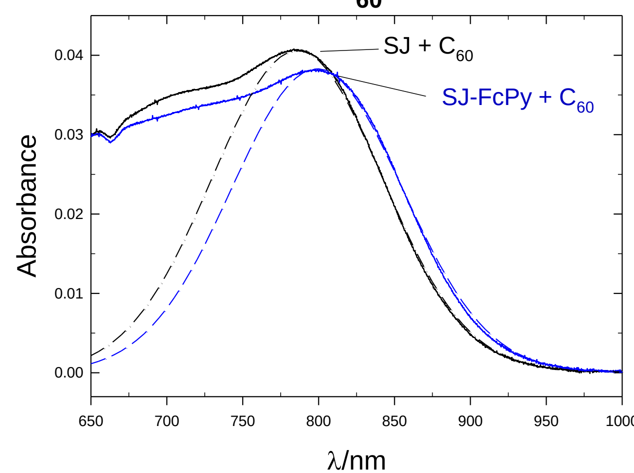
C_{60}



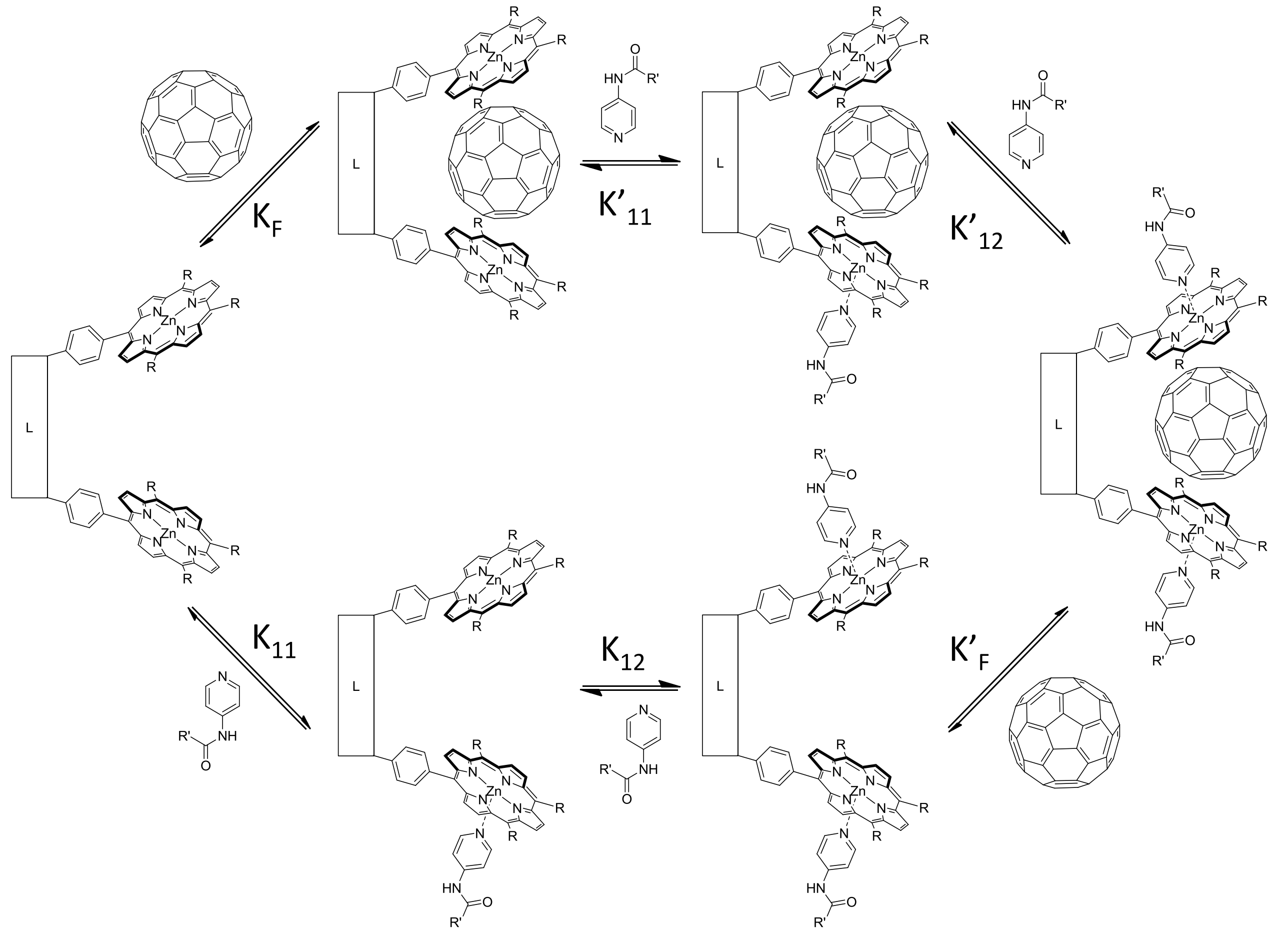
	$SJ+C_{60}$	$SJ\text{-}FcPy + C_{60}$
V	860	724

Toluene

C_{60}



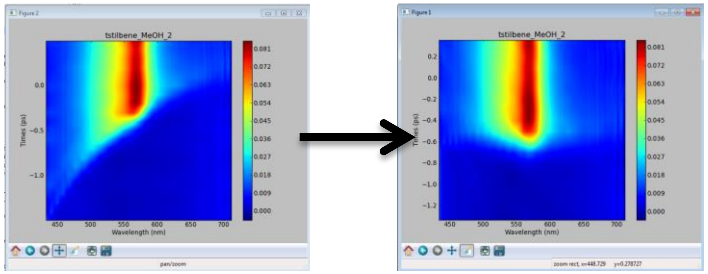
	$SJ+C_{60}$	$SJ\text{-}FcPy + C_{60}$
V	830	774



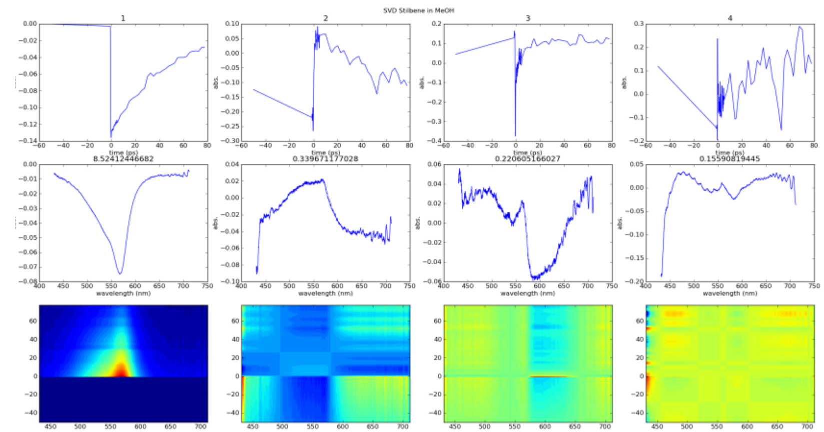
Solvent	K$_F$ (C_{60})	K'$_{11}$	K'$_{12}$			K$_F$ (C_{70})	K'$_{11}$	K'$_{12}$
toluene	17,950	63,063	9,502			214,500	82,250	8,400
cyclohexane	1,815,106	52,068	8,500			4,317,136	148,733	15,085
		K$_{11}$	K$_{12}$	K'$_F$ (C_{60})		K'$_F$ (C_{70})		
toluene		23,650	4,400	25,000		289,500		
cyclohexane		106,398	13,591	188,149		23,094,794		

PyTrA Analysis Package

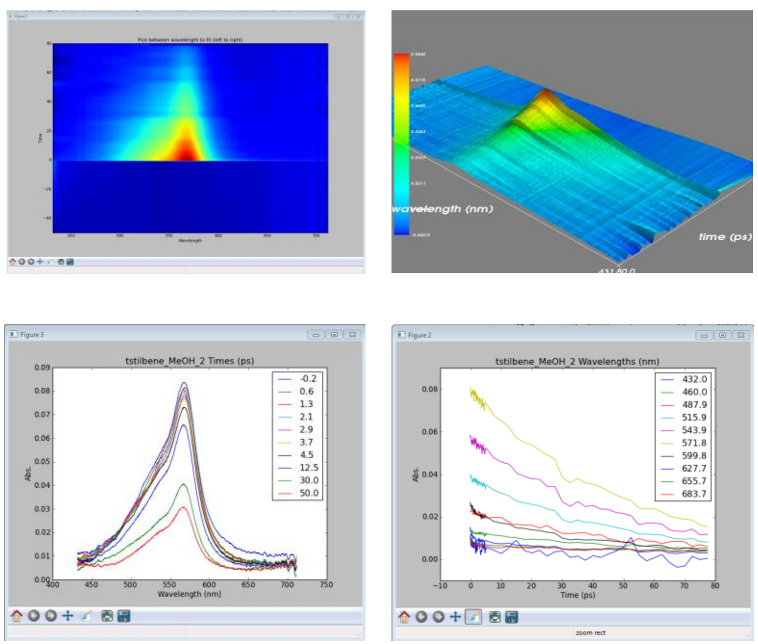
Dispersion correction



Singular value decomposition



Visualization



Markov Chain Monte Carlo