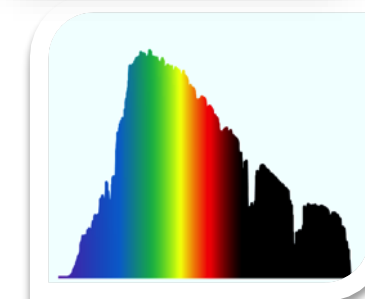
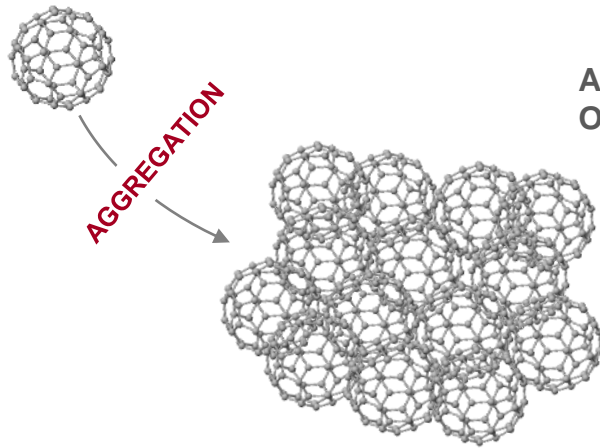


SUSTAINABLE NANOTECHNOLOGY ORGANIZATION CONFERENCE
PEDRO ALVAREZ TRIBUTE SESSION
NOVEMBER 5TH, 2017

FULLERENE: FROM ENVIRONMENTAL IMPLICATION TO DISINFECTION APPLICATION ...AND BEYOND

JAEHONG KIM
DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING
SCHOOL OF ENGINEERING AND APPLIED SCIENCES
YALE UNIVERSITY





AQUEOUS-STABLE C_{60} AGGREGATES
OFTEN REFERRED TO AS nC_{60}

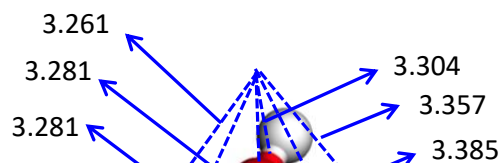
WHY ARE THESE NEGATIVELY CHARGED?

ANY CHARGE TRANSFER FROM WATER MOLECULES?

ONLY WAY TO ANSWER THIS QUESTION: FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY COMPUTATIONS

CHOI ET AL., ENVIRON. SCI. TECHNOL., 2015, 49 (3), 1529–1536

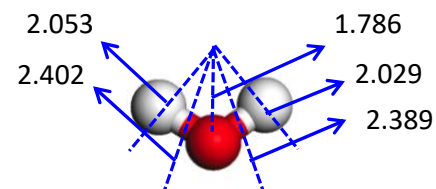
$$DE_{formation} = -2.983 \text{ kcal/mol}$$



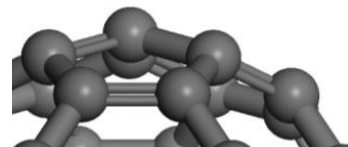
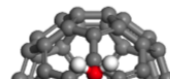
HEXAGONAL SITE



$$DE_{formation} = -2.305 \text{ kcal/mol}$$



PENTAGONAL SITE

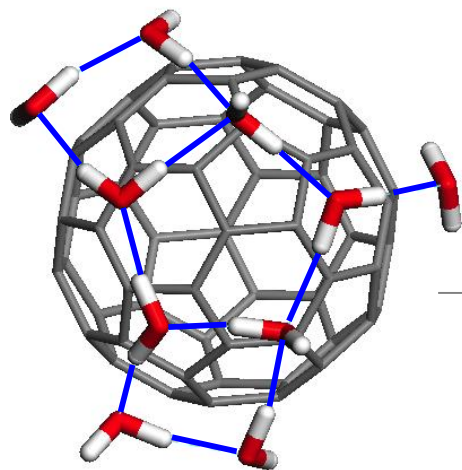


INTERACTION OF THE LONE PAIR OF ELECTRONS OF **OXYGEN** WITH π^* -ORBITALS OF C_{60}
(RATHER THAN A HYDROGEN BONDING INTERACTION AS IN THE CASE OF BENZENE)

C_{60} ACQUIRES A **PARTIAL NEGATIVE CHARGE** FROM WATER MOLECULE.

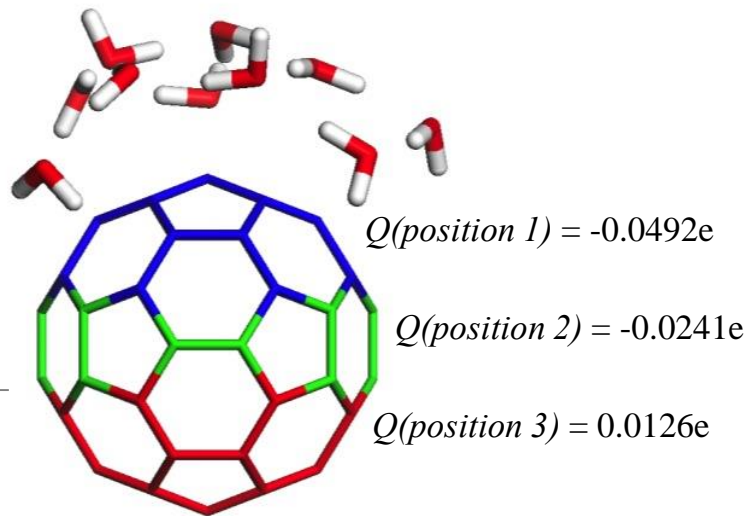
HYDROGEN BOND NETWORK OF 10 WATER MOLECULES ON SINGLE C₆₀

CHOI ET AL., ENVIRON. SCI. TECHNOL., 2015, 49 (3), 1529–1536



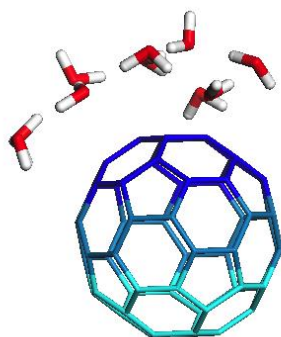
**MOST (83%) OF FORMATION ENERGY
FOR C₆₀-10H₂O CLUSTER RESULTS FROM
INTERACTION AMONG WATER MOLECULES**

C₆₀ CAN BE **POLARIZED** BY WATER
MOLECULES, POTENTIALLY ENHANCING
THE SOLVATION OF C₆₀ BY WATER



C₆₀ DIMER PARTIALLY SOLVATED BY WATER

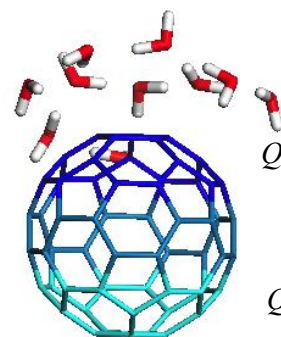
CHOI ET AL., ENVIRON. SCI. TECHNOL., 2015, 49 (3), 1529–1536



$$Q(\text{position 1}) = -0.0481e$$

$$Q(\text{position 2}) = -0.0037e$$

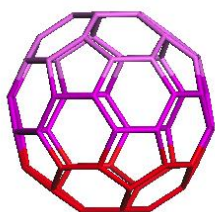
$$Q(\text{position 3}) = -0.0027e$$



$$Q(\text{position 1}) = -0.0406e$$

$$Q(\text{position 2}) = -0.0030e$$

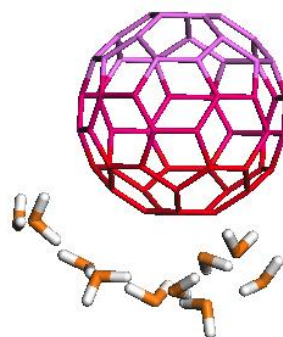
$$Q(\text{position 3}) = -0.0119e$$



$$Q(\text{position 4}) = -0.0164e$$

$$Q(\text{position 5}) = 0.0166e$$

$$Q(\text{position 3}) = 0.0010e$$



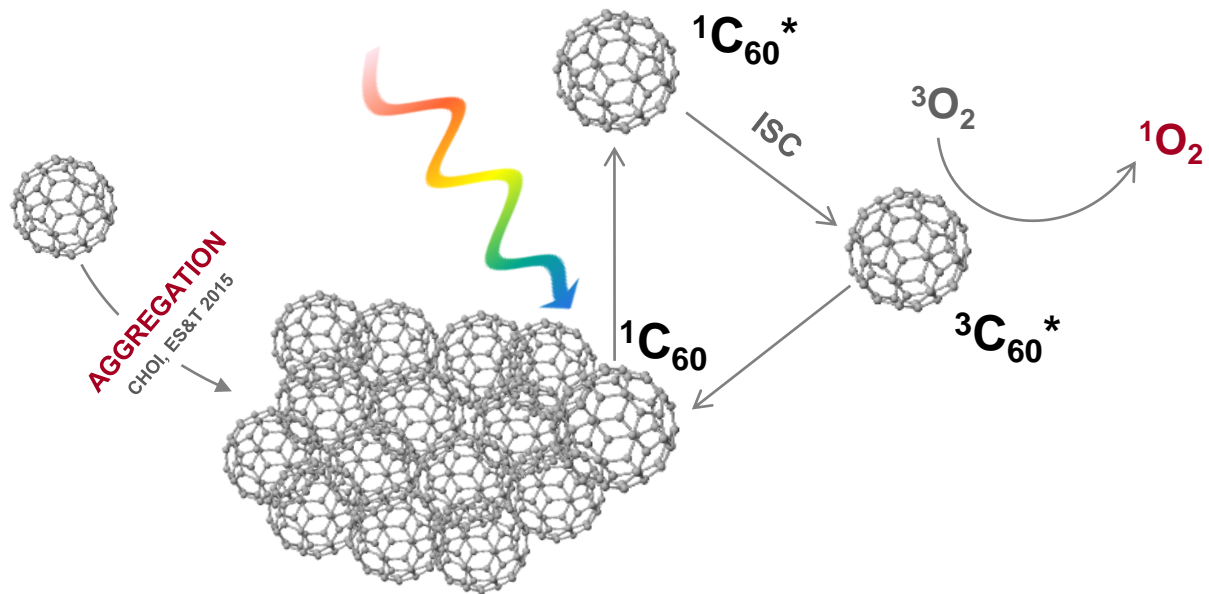
$$Q(\text{position 4}) = -0.0116e$$

$$Q(\text{position 5}) = -0.0026e$$

$$Q(\text{position 3}) = -0.0409e$$

PRESENCE OF ANOTHER C₆₀ HAS **NEGLIGIBLE EFFECT** ON THE **HYDROGEN BONDING NETWORK FORMATION** AND THE **CHARGE TRANSFER** FROM WATER MOLECULES TO C₆₀

THIS POLARIZATION OF THE TWO C₆₀S LIKELY **ENHANCES THE STRENGTH OF THE C₆₀-C₆₀ INTERACTION** VIA ELECTROSTATIC ATTRACTION BETWEEN OPPOSITE CHARGES



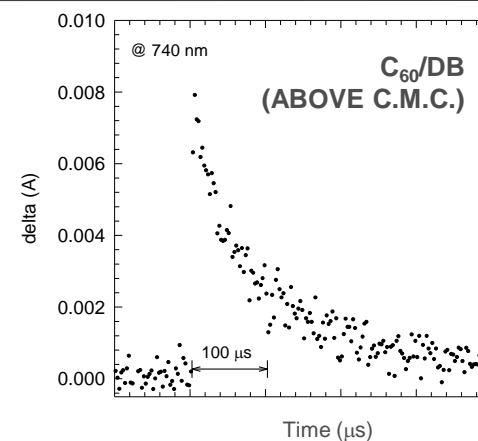
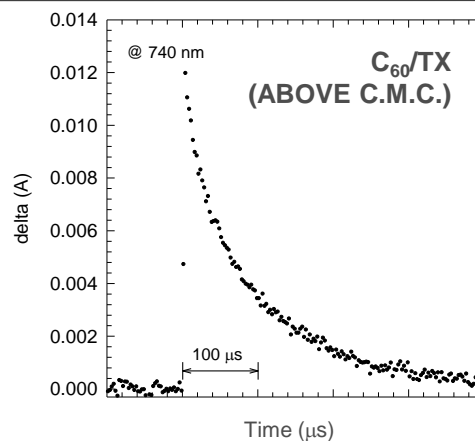
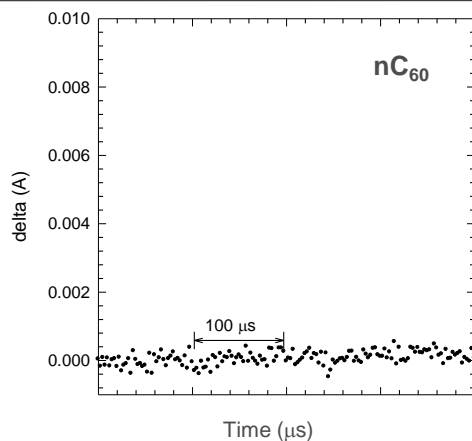
**¹O₂ CLAIMED TO BE
RESPONSIBLE FOR CELL "DEATH"**

IS THAT TRUE?

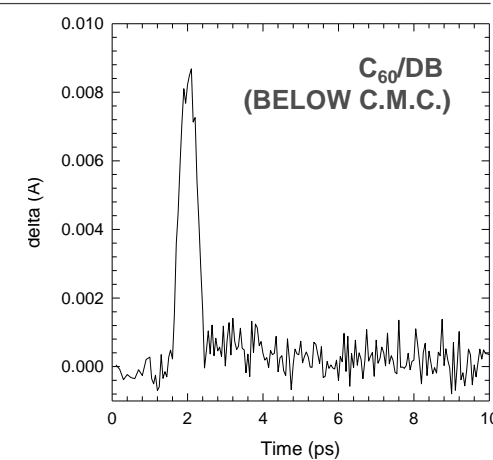
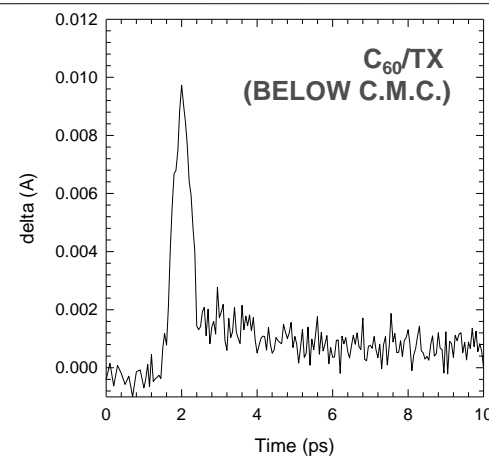
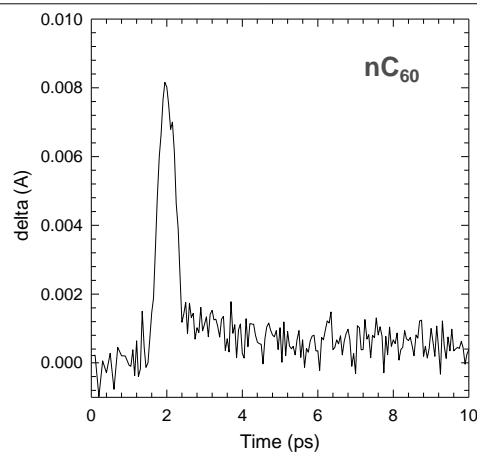
C₆₀ AGGREGATES ARE NOT VERY PHOTOACTIVE

LEE ET AL., *ENVIRON. SCI. TECHNOL.*, 2007, 41, 2529-2535
LEE AND KIM, *ENVIRON. SCI. TECHNOL.*, 2008, 42, 1552-1557
LEE ET AL., *ENVIRON. SCI. TECHNOL.*, 2008, 42, 3459-3464

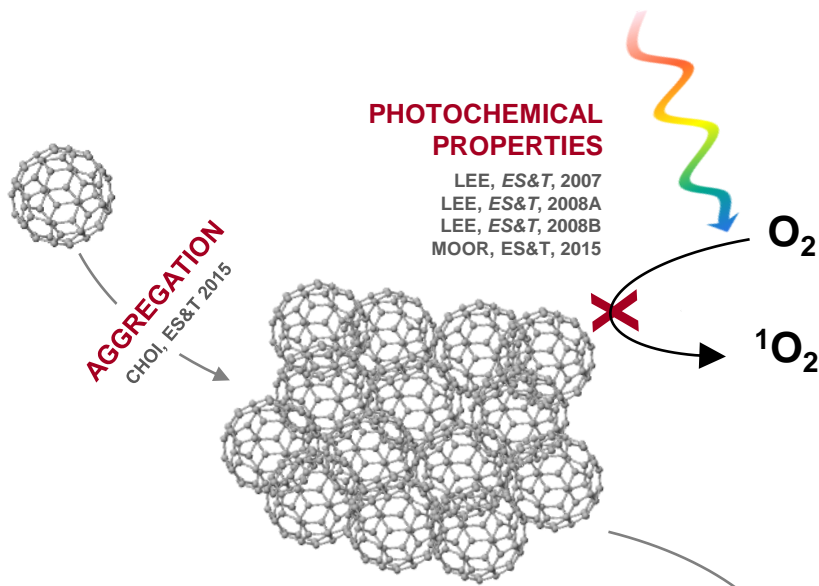
NANO-SECOND LASER FLASH PHOTOLYSIS



FEMTO-SECOND LASER FLASH PHOTOLYSIS



PHOTOCHEMICAL PROPERTY CHANGES A LOT DEPENDING ON AQUEOUS DISPERSION STATE



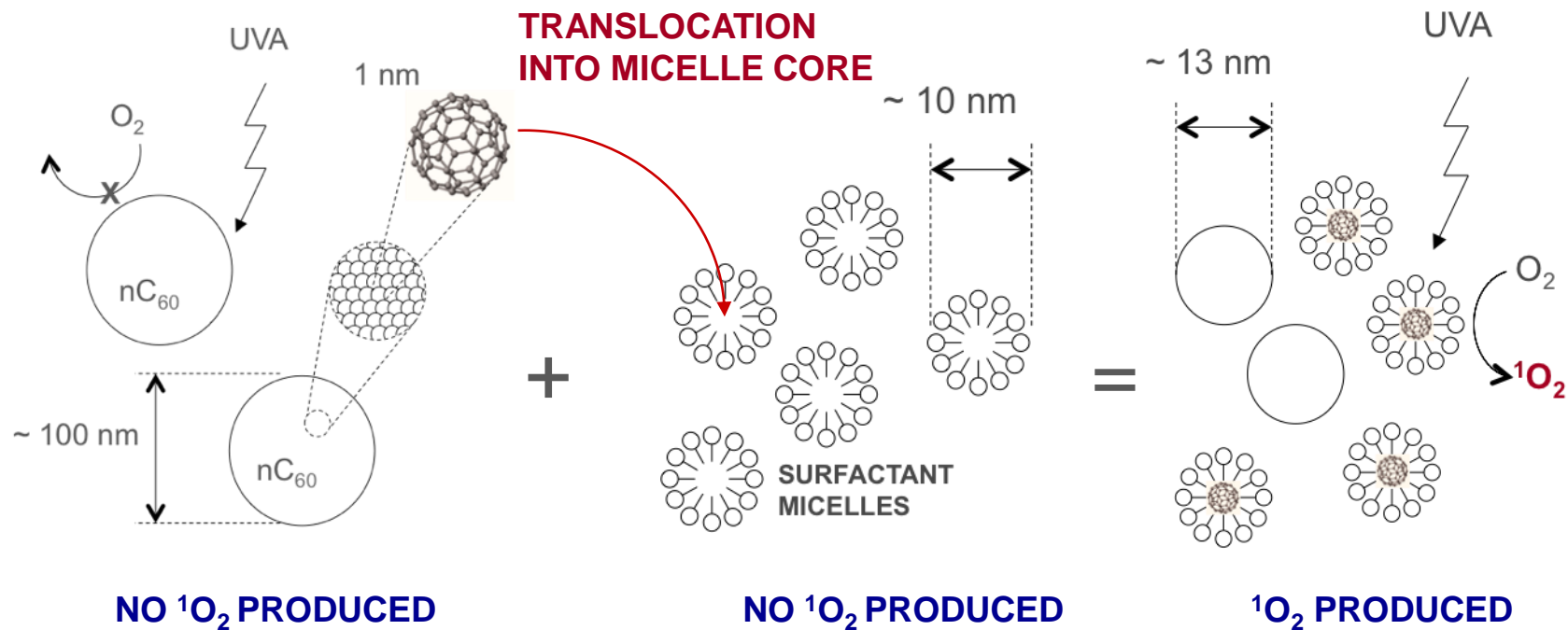
**...OR SOMETHING OTHER
THAN C₆₀ IS INVOLVED IN
CELL TOXICITY?**

**PERHAPS THERE IS A WAY
FOR C₆₀ TO GET INTO CELLS
IN MOLECULAR FORM?**

?

C₆₀ IN C₆₀ AGGREGATES CAN MOVE INTO MICELLES

ZHANG ET AL, *ENVIRON. SCI. TECHNOL.*, 2009, 43, 9124-9129



SOME OTHER PIECES OF EVIDENCE

CHANGE IN UV-VIS ABSORPTION SPECTRA

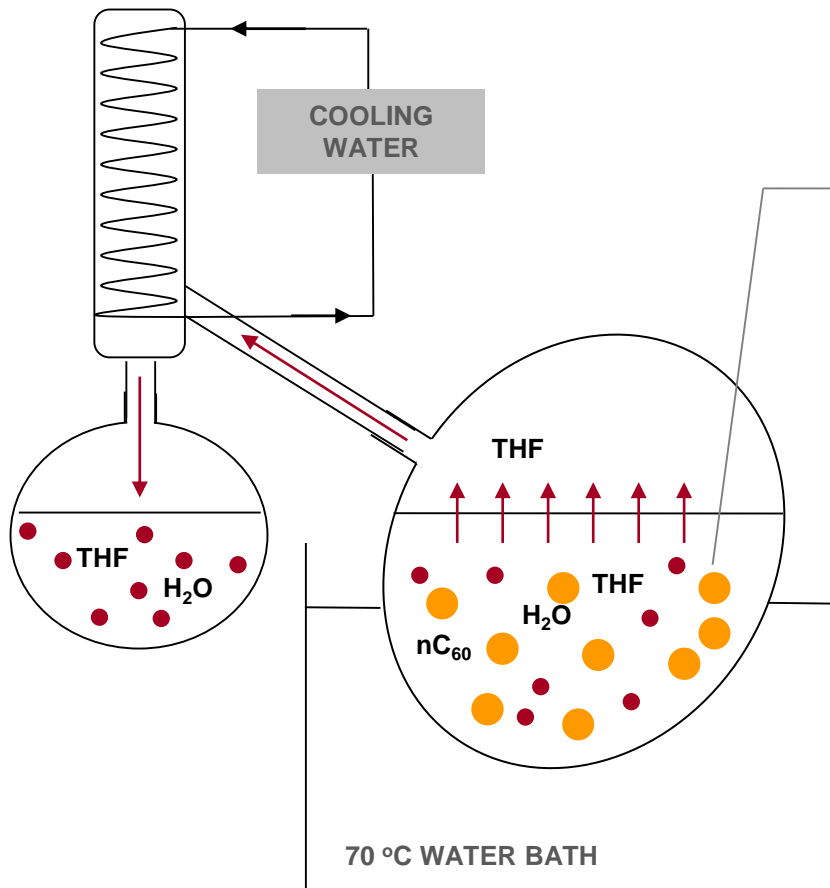
CHANGE IN SURFACTANT MICELLE FLUORESCENCE SPECTRA

PARTICLE STABILITY (WITH MgClO₄ ADDITION)

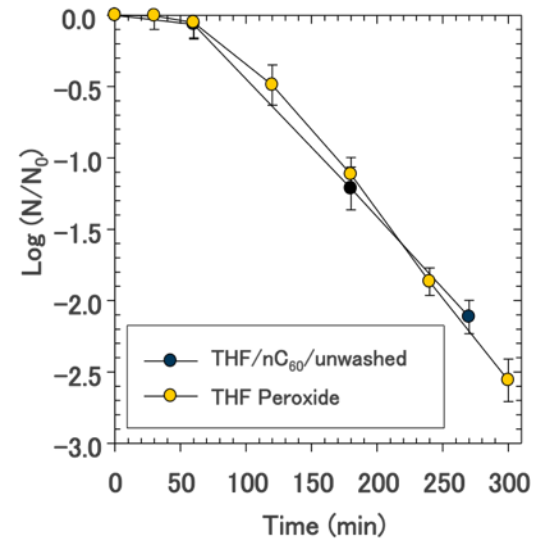
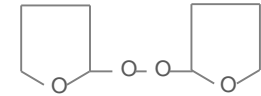
TEM IMAGE ANALYSIS

THERE IS SOMETHING SMELLY IN THE SOUP

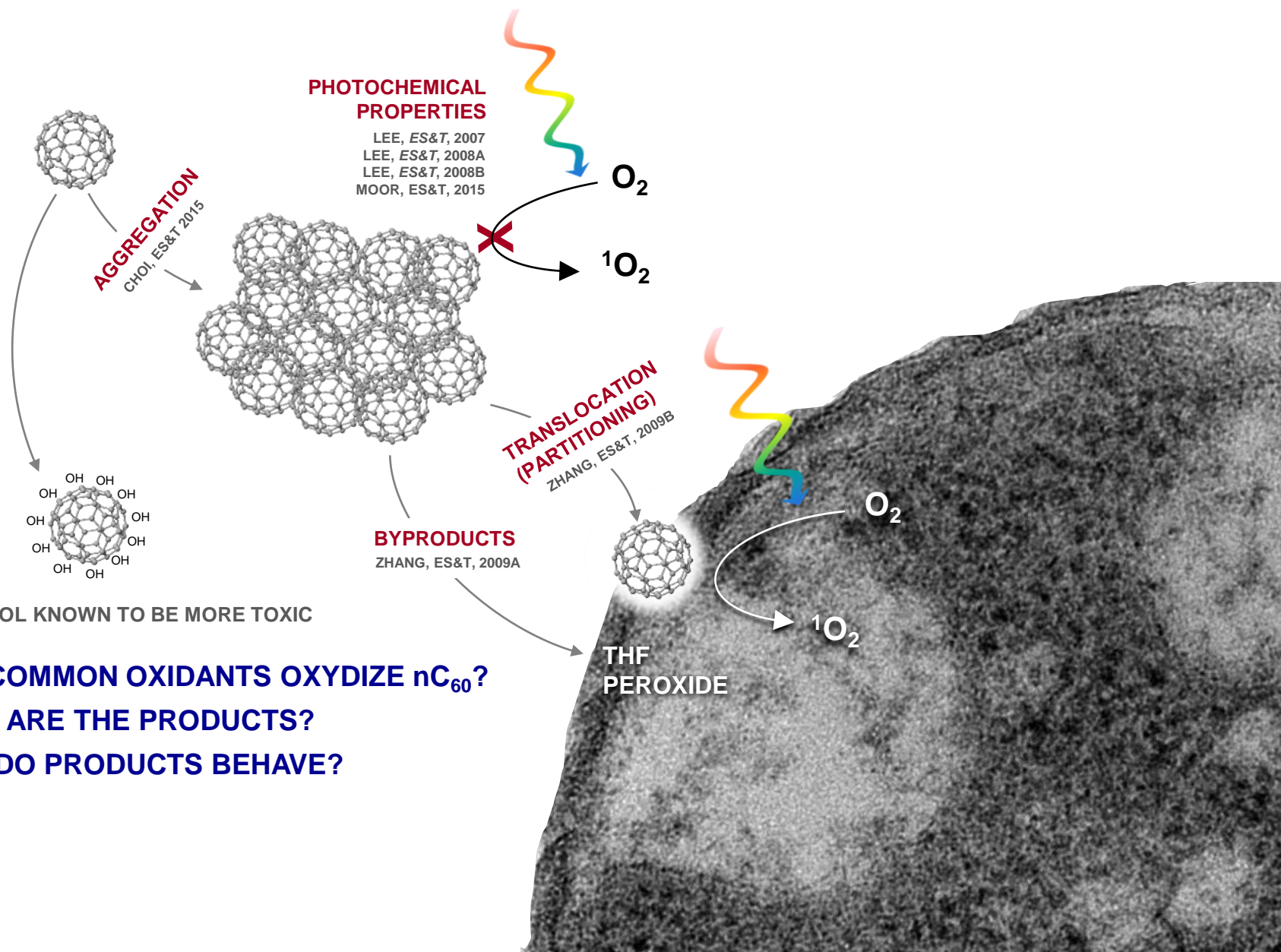
ZHANG ET AL., ENVIRON. SCI. TECHNOL., 2009, 43, 108-113



E. COLI INACTIVATION WAS MOSTLY DUE TO THF PEROXIDE



THF/nC₆₀ HAS BEEN CONSISTENTLY REPORTED TO BE MORE TOXIC THAN OTHER FORMS OF nC₆₀



nC_{60} IN WATER CAN BE OXIDIZED BY O_3 , OH , e^-_{aq} , AND UVC FORMING A WIDE RANGE OF OXYDIZED FULLERENES

FORTNER ET AL., ENVIRON. SCI. TECHNOL., 2007, 41, 7497-7502

LEE ET AL., ENVIRON. SCI. TECHNOL., 2009, 43, 4878-4883

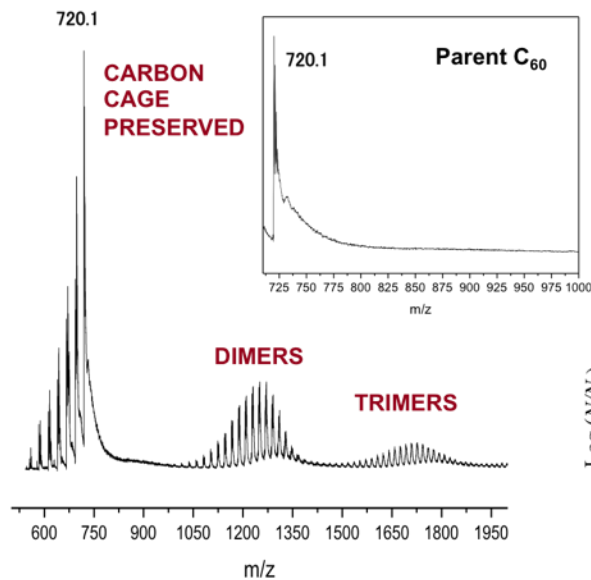
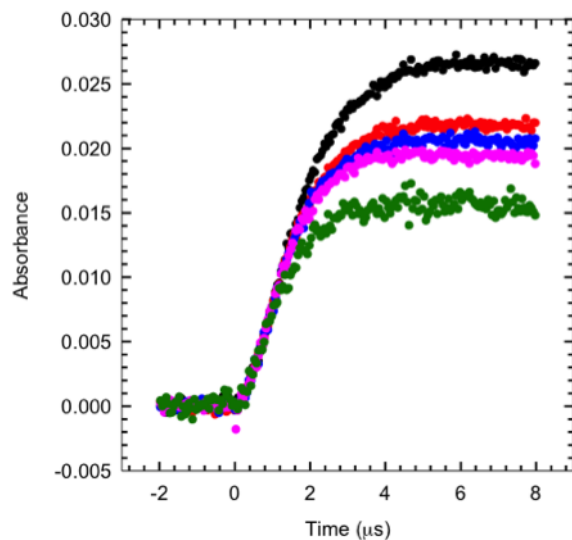
CHO ET AL., ENVIRON. SCI. TECHNOL., 2009, 43, 7410-7415

LEE ET AL., ENVIRON. SCI. TECHNOL., 2010, 44, 3786-3792

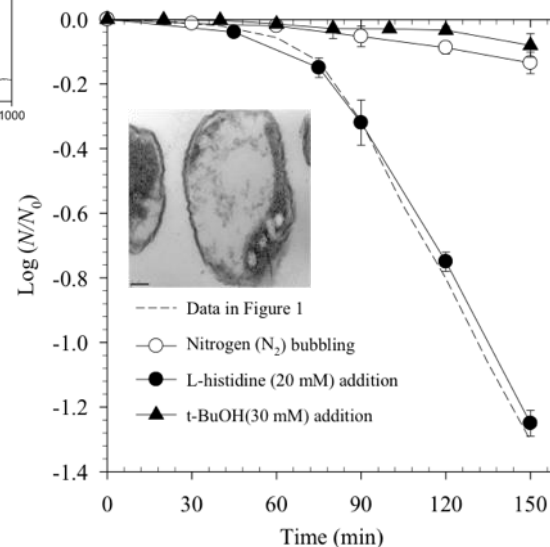
CHO ET AL., ENVIRON. SCI. TECHNOL., 2011, 45, 9627-9633

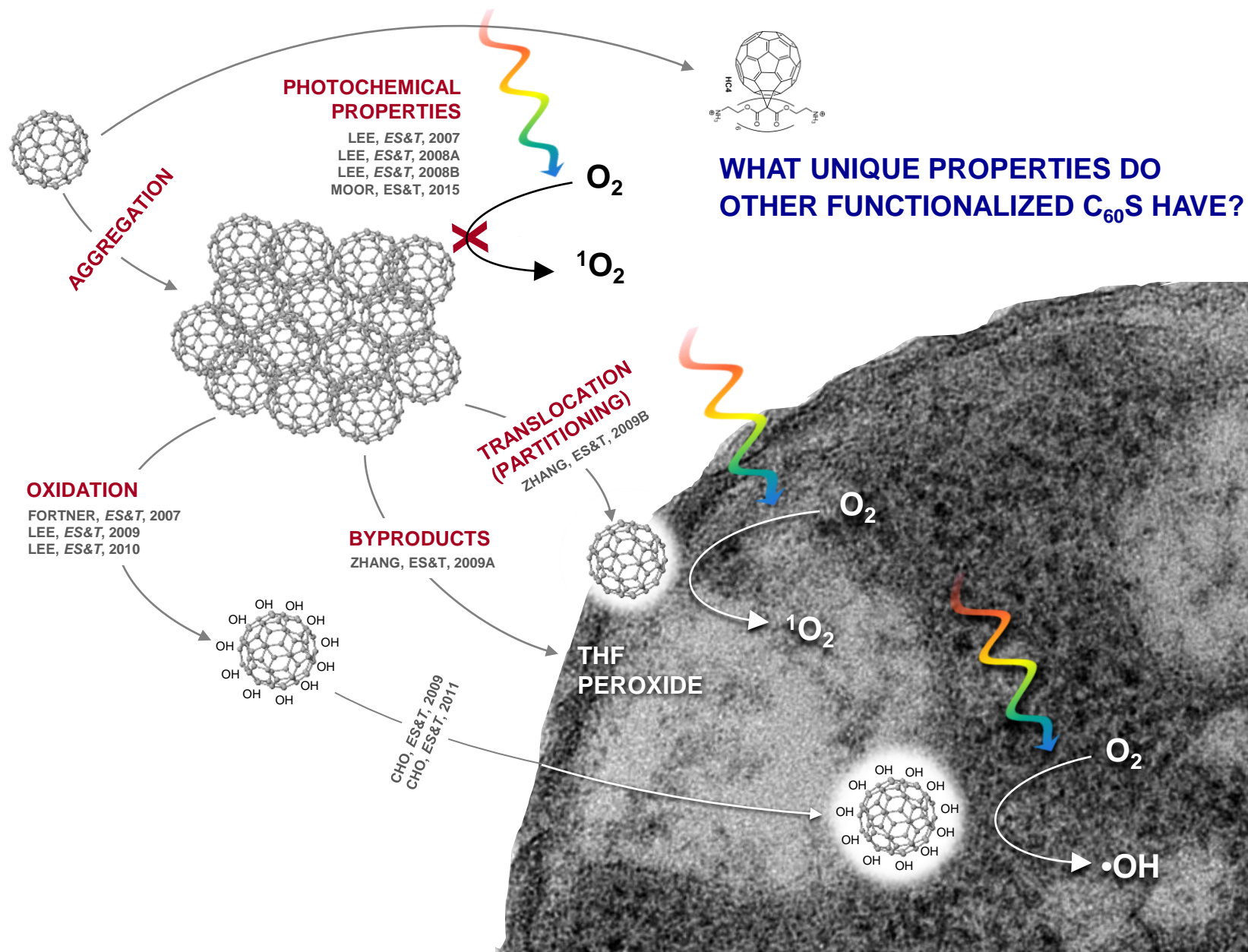
PRODUCT CHARACTERIZATION

REACTION KINETICS



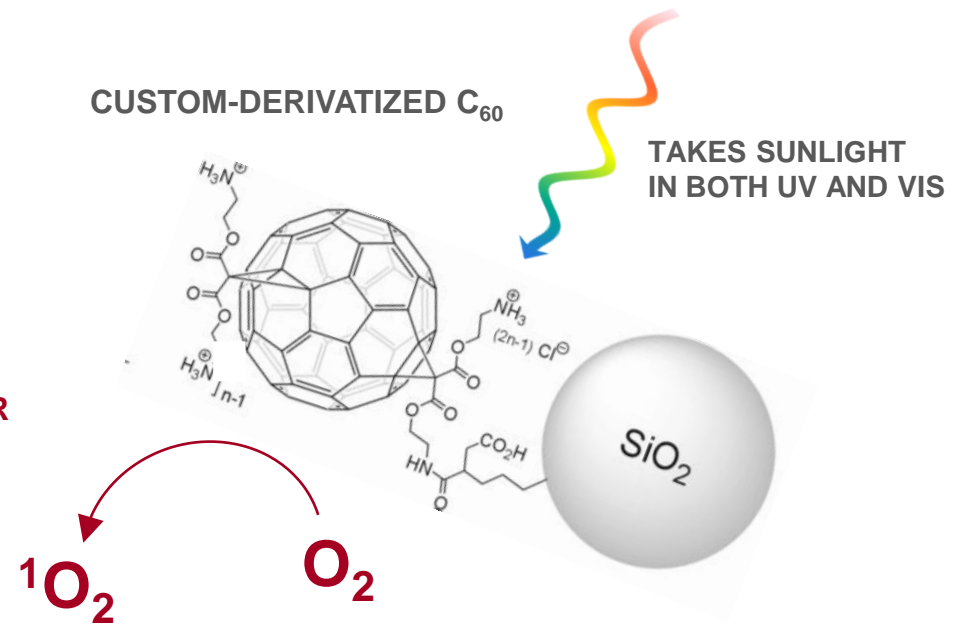
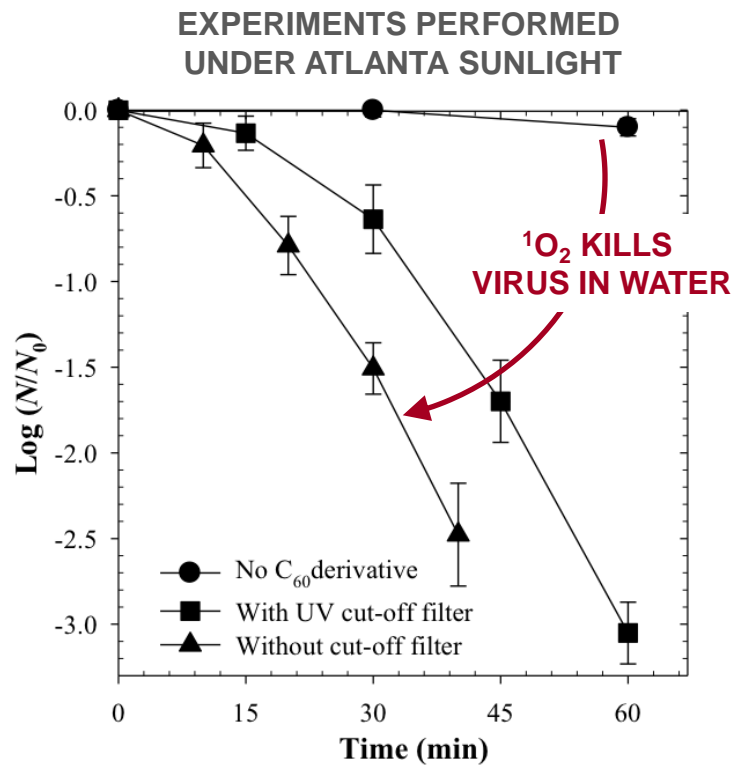
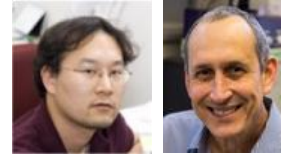
INACTIVATION KINETICS AND MECHANISMS





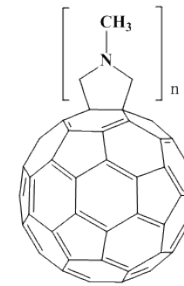
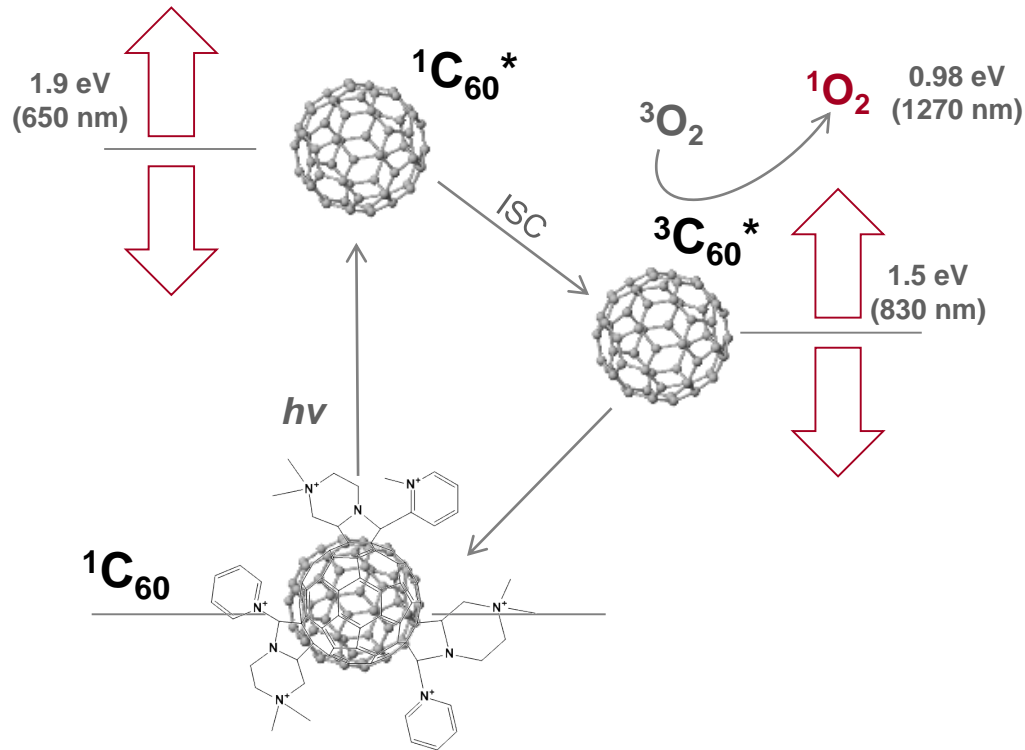
AMINE-FUNCTIONALIZED C₆₀ IS AN EFFICIENT VIRUS KILLER

LEE ET AL., *ENVIRON. SCI. TECHNOL.*, 2009, 43, 6604-6610
CHO ET AL., *ENVIRON. SCI. TECHNOL.*, 2010, 44, 6685-6691
LEE ET AL., *ENVIRON. SCI. TECHNOL.*, 2010, 44, 9488-9495
LEE ET AL., *ENVIRON. SCI. TECHNOL.*, 2011, 45, 10598-10604

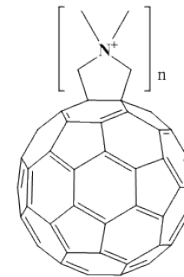


LET'S TAKE A LITTLE CLOSER LOOK

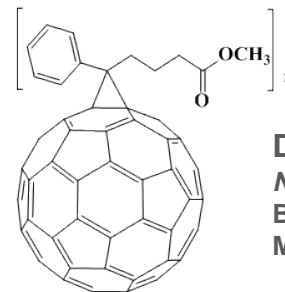
IF WE UNDERSTAND THE EFFECT OF FUNCTIONALIZATION MORE,
WE SHOULD BE ABLE TO BETTER ASSESS THEIR ENVIRONMENTAL IMPACT
AND MORE EFFECTIVELY ENGINEER THEM FOR ENVIRONMENTAL APPLICATION



DERIVATIVE A
N-METHYLFULLERO
PYRROLIDINE

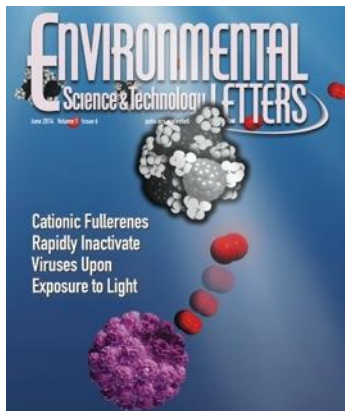


DERIVATIVE B
N-METHYLFULLERO
PYRROLIDIUM ION



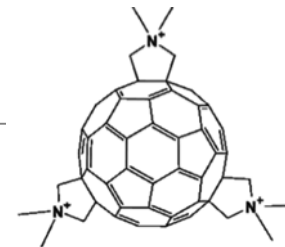
DERIVATIVE C (PCBM)
N-PHENYL-C(60+N)-
BUTYRIC ACID
METHYL ESTER

INTERMEDIATE STATE ENERGIES
SIZE / SURFACE AREA / DIFFUSION LIMITATIONS
SELF-QUENCHING (CRYSTALLINITY)

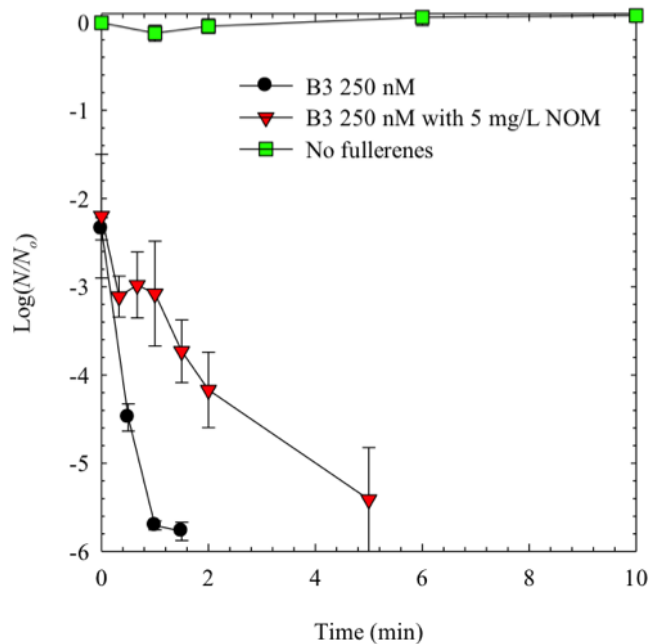


ONE OF CATIONIC FULLERENE AGGREGATES SHOWED UNPRECEDENTED VIRUS PHOTOINACTIVATION EFFICIENCIES IN WATER

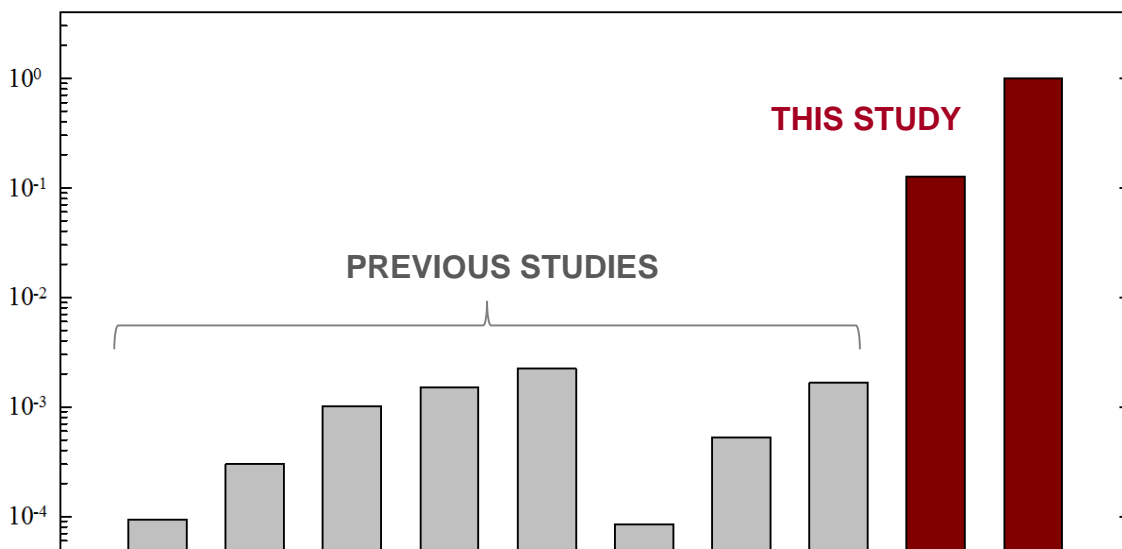
SNOW ET AL., ENVIRON. SCI. TECHNOL. LETTERS, 2014, 1, 290-294



MS2 INACTIVATION UNDER SUNLIGHT

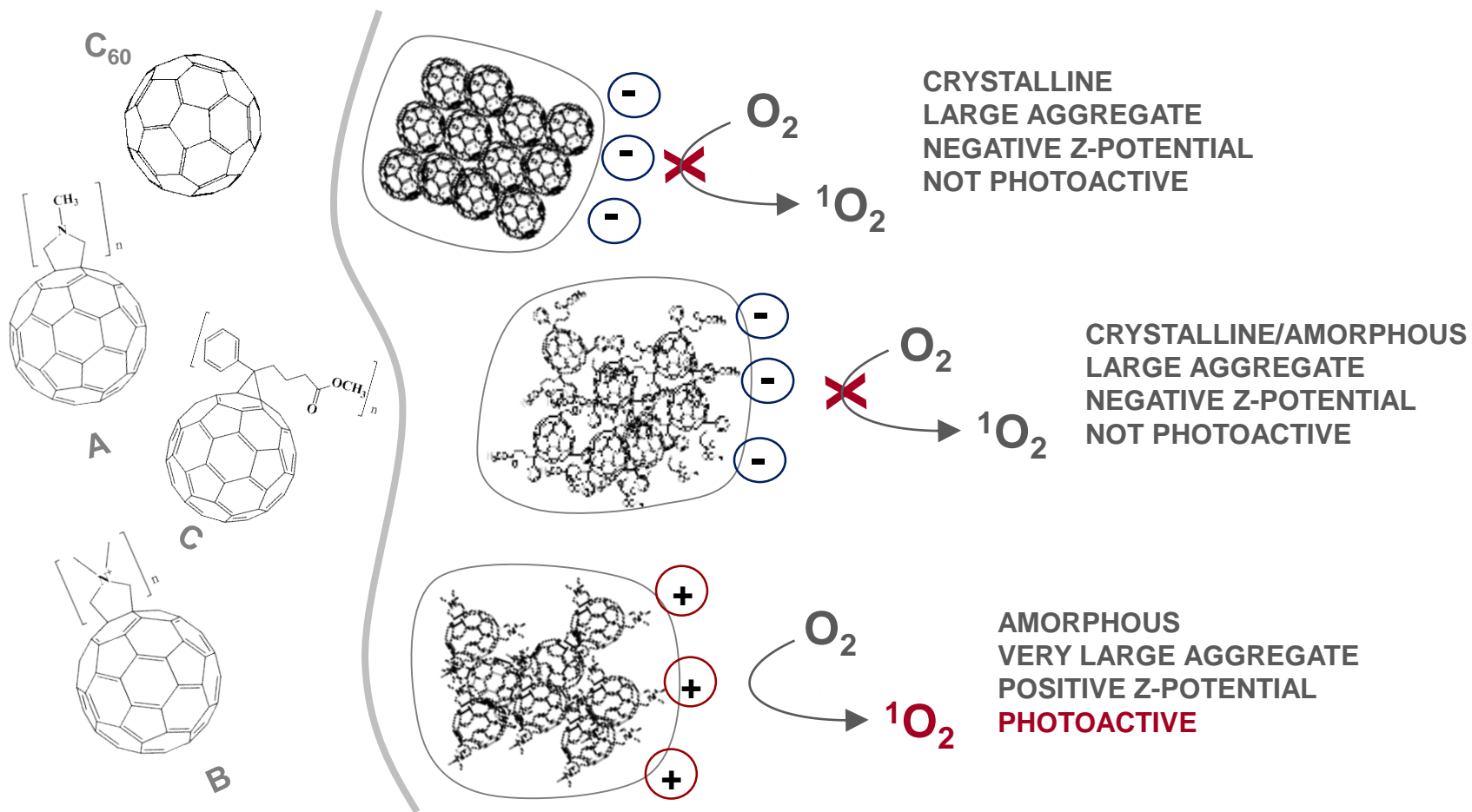


MS2 INACTIVATION NORMALIZED BY SENSITIZER CONCENTRATION



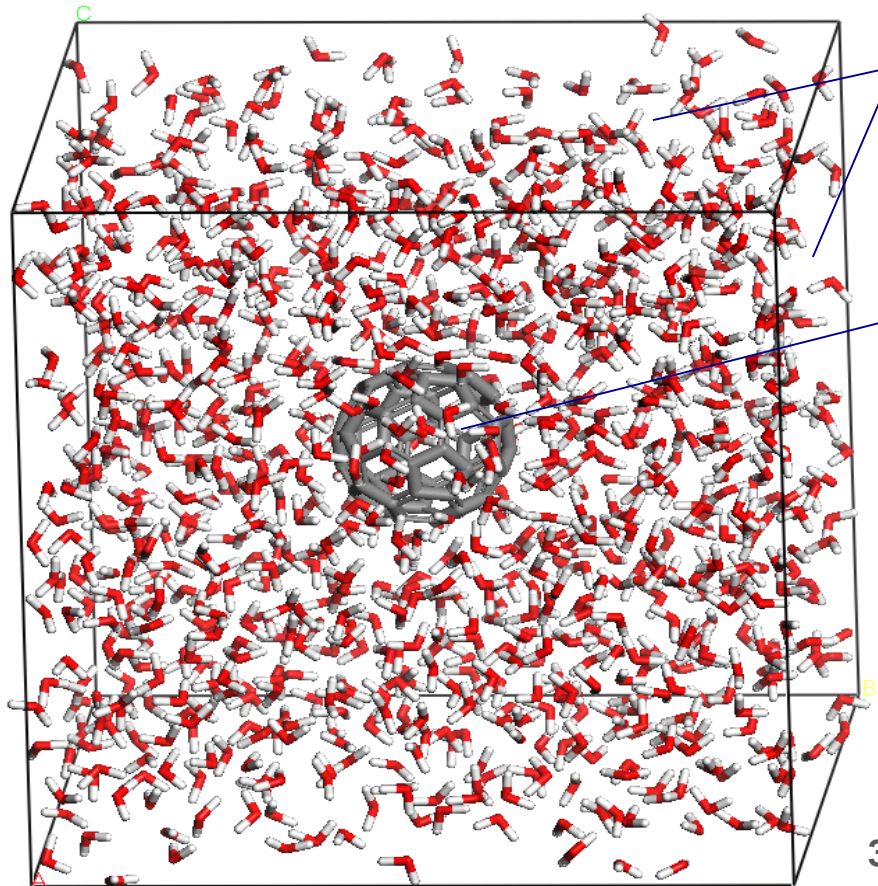
THE PHOTOACTIVITY OF FULLERENE AGGREGATES DO NOT NECESSARILY DEPEND ON AGGREGATE CRYSTALLINITY OR SIZE

SNOW ET AL., ENVIRON. SCI. TECHNOL., 2012, 46, 13227-13234



IF EXPERIMENTS ARE ALL DONE
BUT ANSWERS ARE NOT STILL FOUND...
TALK TO YOUR COMPUTATIONAL COLLEAGUES

MOLECULAR DYNAMICS SIMULATION



1,000 H₂O MOLECULES

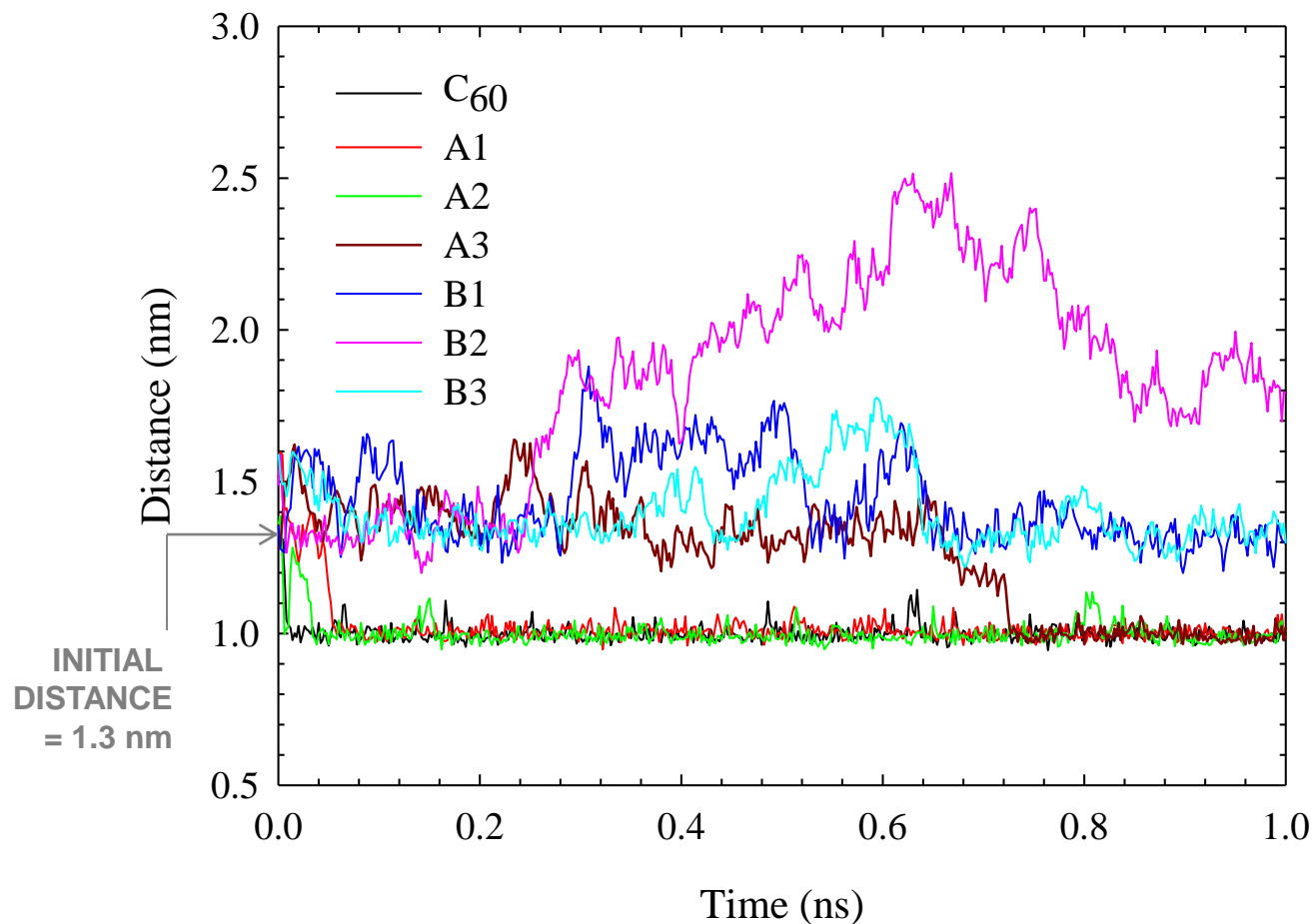
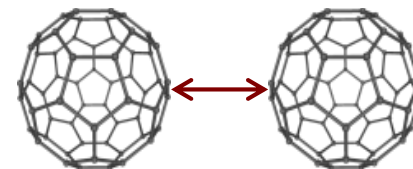
ONE OR TWO FULLERENE MOLECULES

SIMULATION PERFORMED UNDER
298 K AND 1 ATM
FOR 1-2 NANoseconds

30 Å × 30 Å × 30 Å CUBIC CELL

FULLERENE-FULLERENE INTERACTION

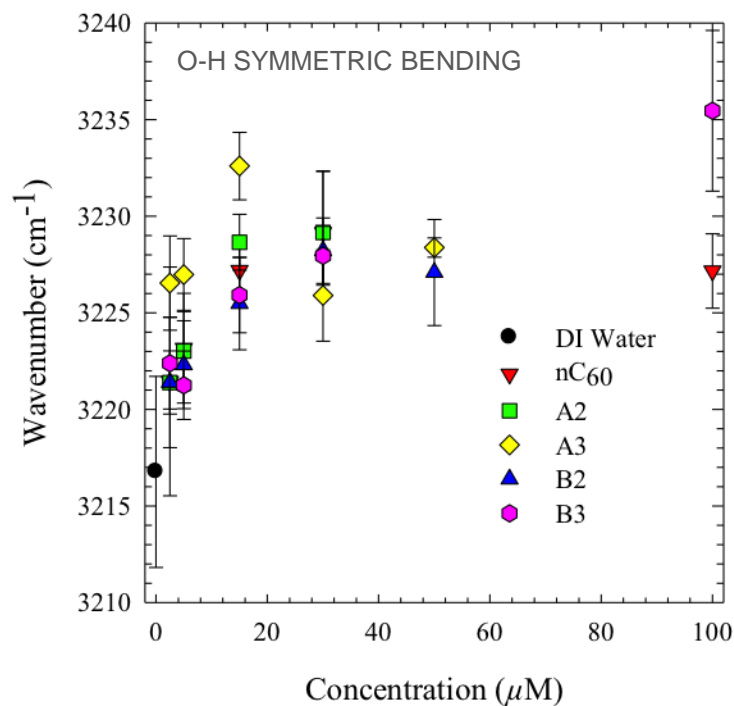
INTERACTION DISTANCES



SIGNIFICANTLY
WEAKER
INTERACTIONS
BETWEEN
B SERIES
FULLERENES

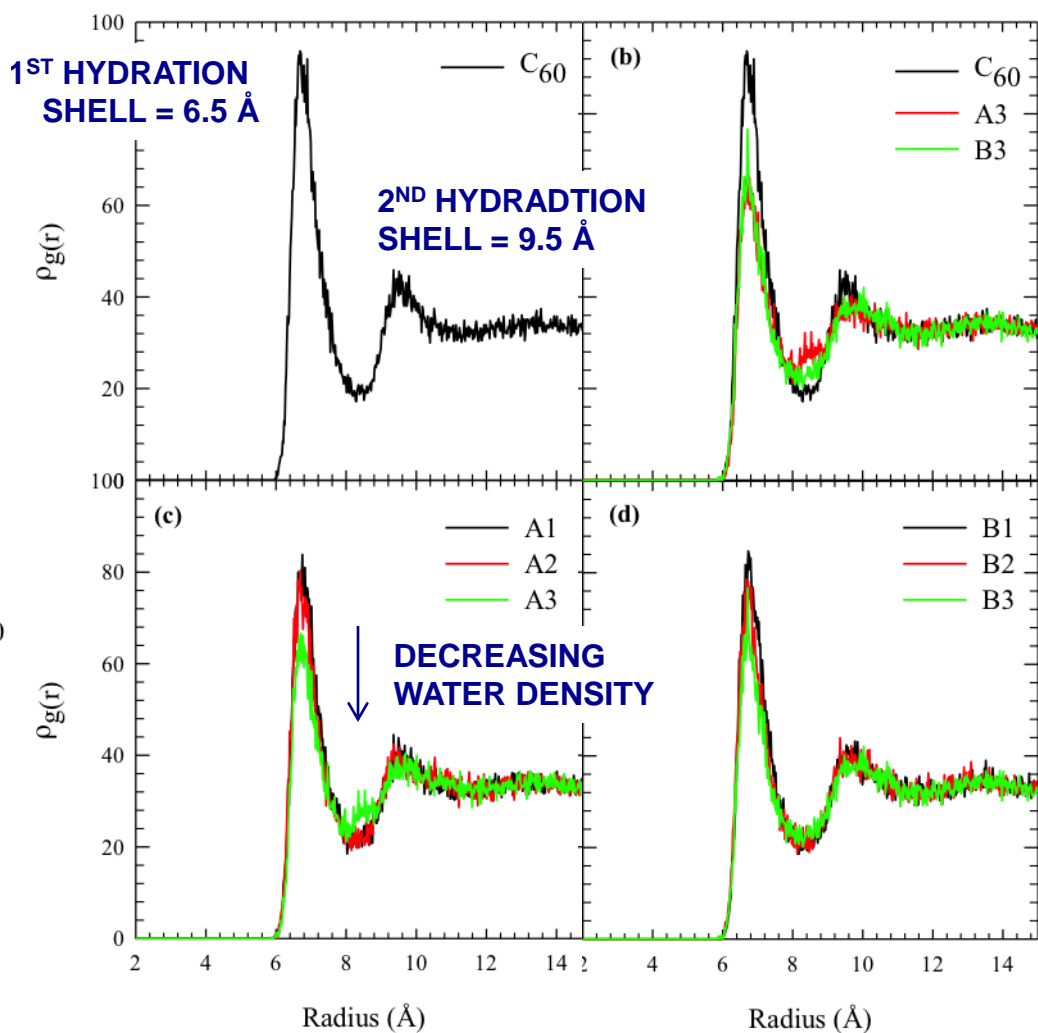
FULLERENE-WATER INTERACTION

RAMAN SPECTROSCOPY



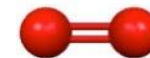
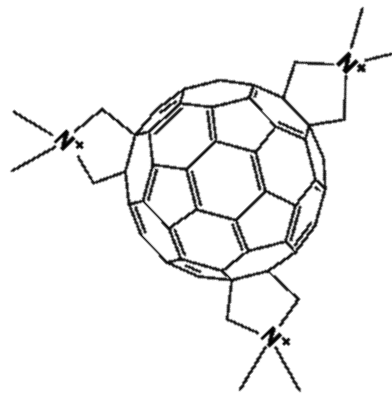
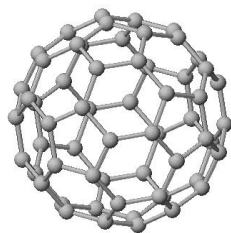
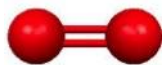
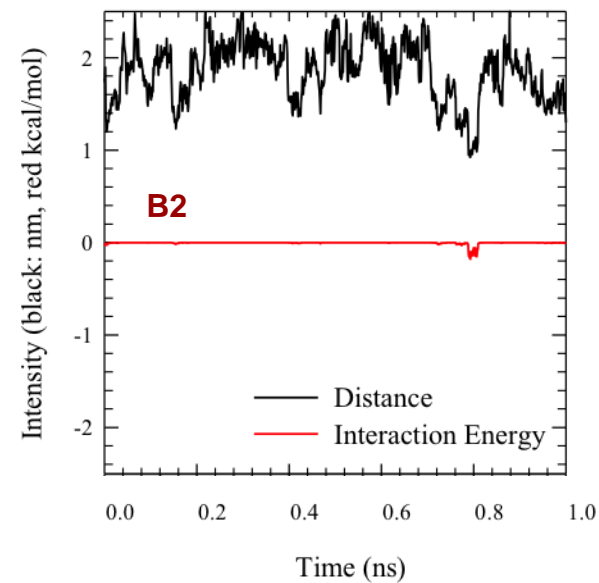
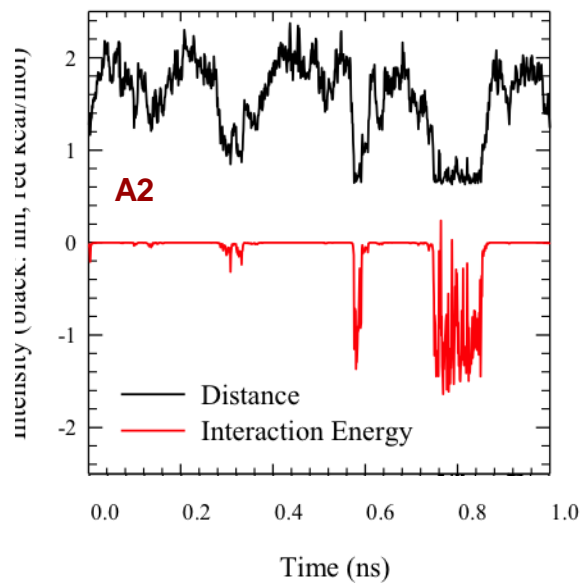
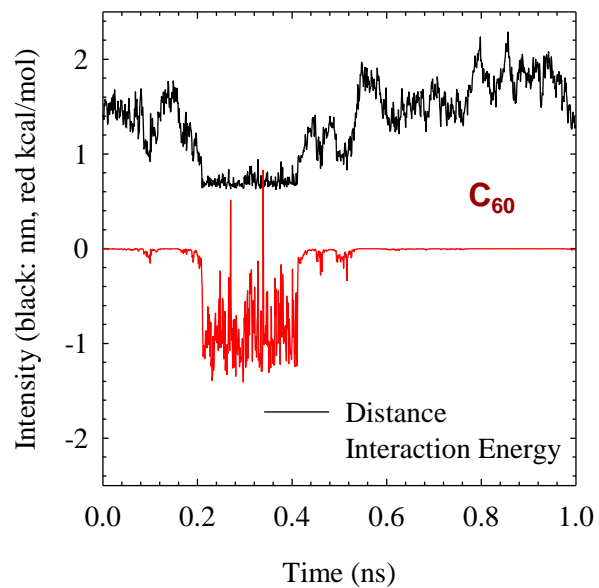
**MORE STRUCTURED
HYDRATION ENVIRONMENT**

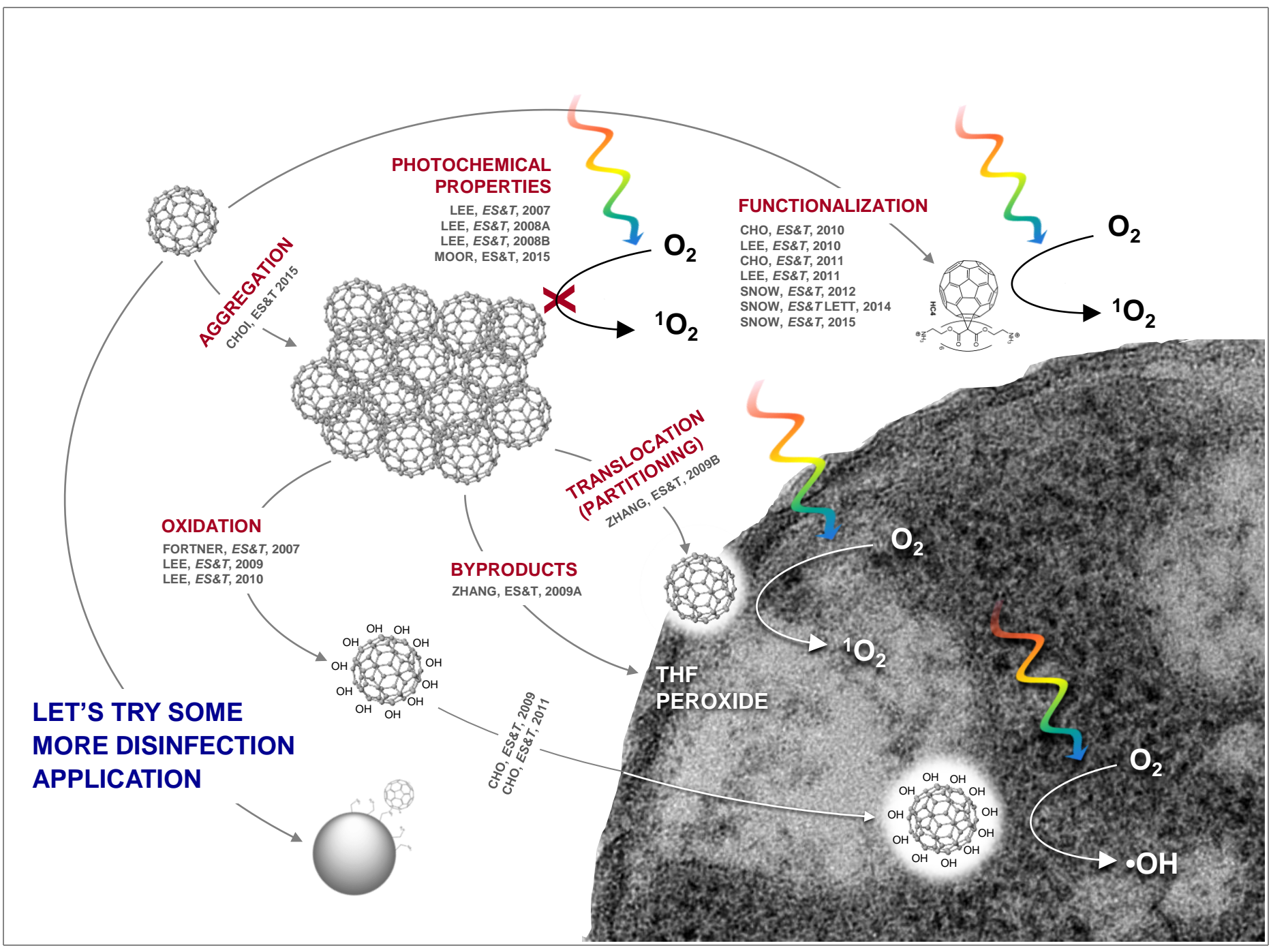
RADIAL DISTRIBUTION FUNCTION



FULLERENE-OXYGEN INTERACTION

INTERACTION ENERGIES





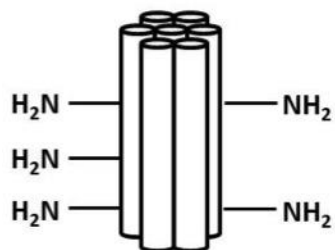
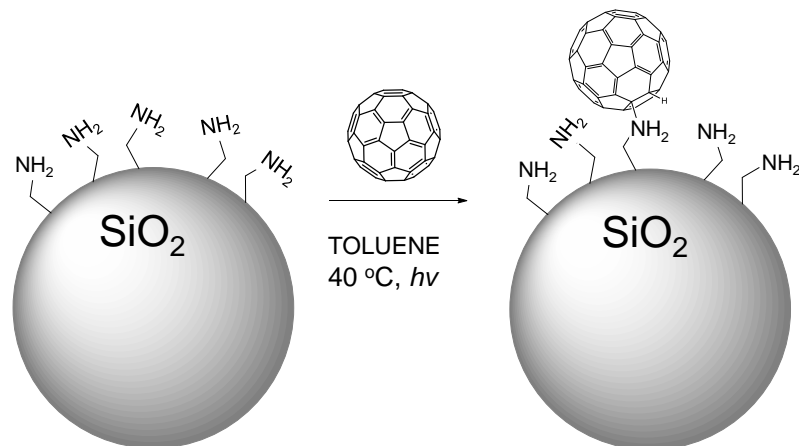
MORE ATTEMPTS ON IMPROVING DISINFECTION EFFICIENCY

MOOR AND KIM, *ENVIRON. SCI. TECHNOL.*, 2014, 48, 2785-2791

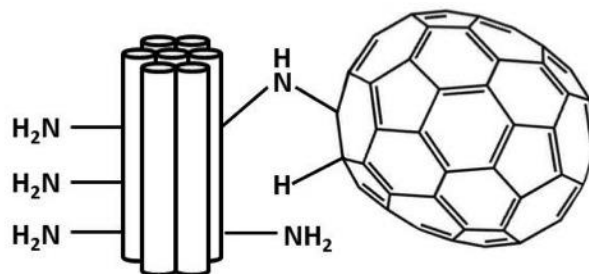
MOOR ET AL., *ENVIRON. SCI. TECHNOL.*, 2015, 49, 5990-5998

MOOR ET AL., *ENVIRON. SCI. TECHNOL.*, 2015, 49, 6190-6197

SIMPLE ONE STEP SYNTHESIS
NUCLEOPHILIC ADDITION OF A TERMINAL AMINE
ACROSS A [6,6] FULLERENE DOUBLE BOND



fullerene
40 °C



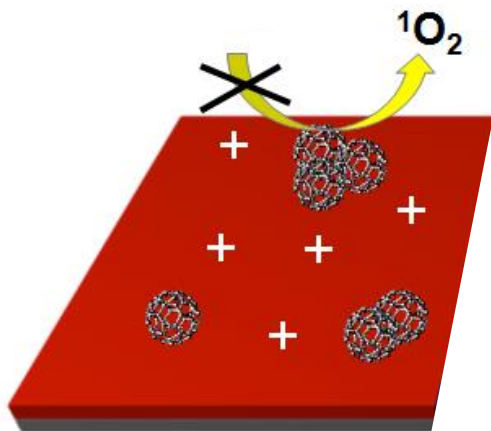
MORE SURFACE AREA
USING MCM41

MORE PHOTOACTIVITY
USING C₇₀

HOW CAN WE MANIPULATE THE LENGTH SCALE OF FULLERENE INCORPORATION ONTO A SUBSTRATE?

PROPERLY SPACED

PREVENT SIGNIFICANT AGGREGATION AND FULLERENE SELF-QUENCHING
INTRODUCE CHEMICAL DISPARATE FUNCTIONALITY



NO LENGTH CONTROL

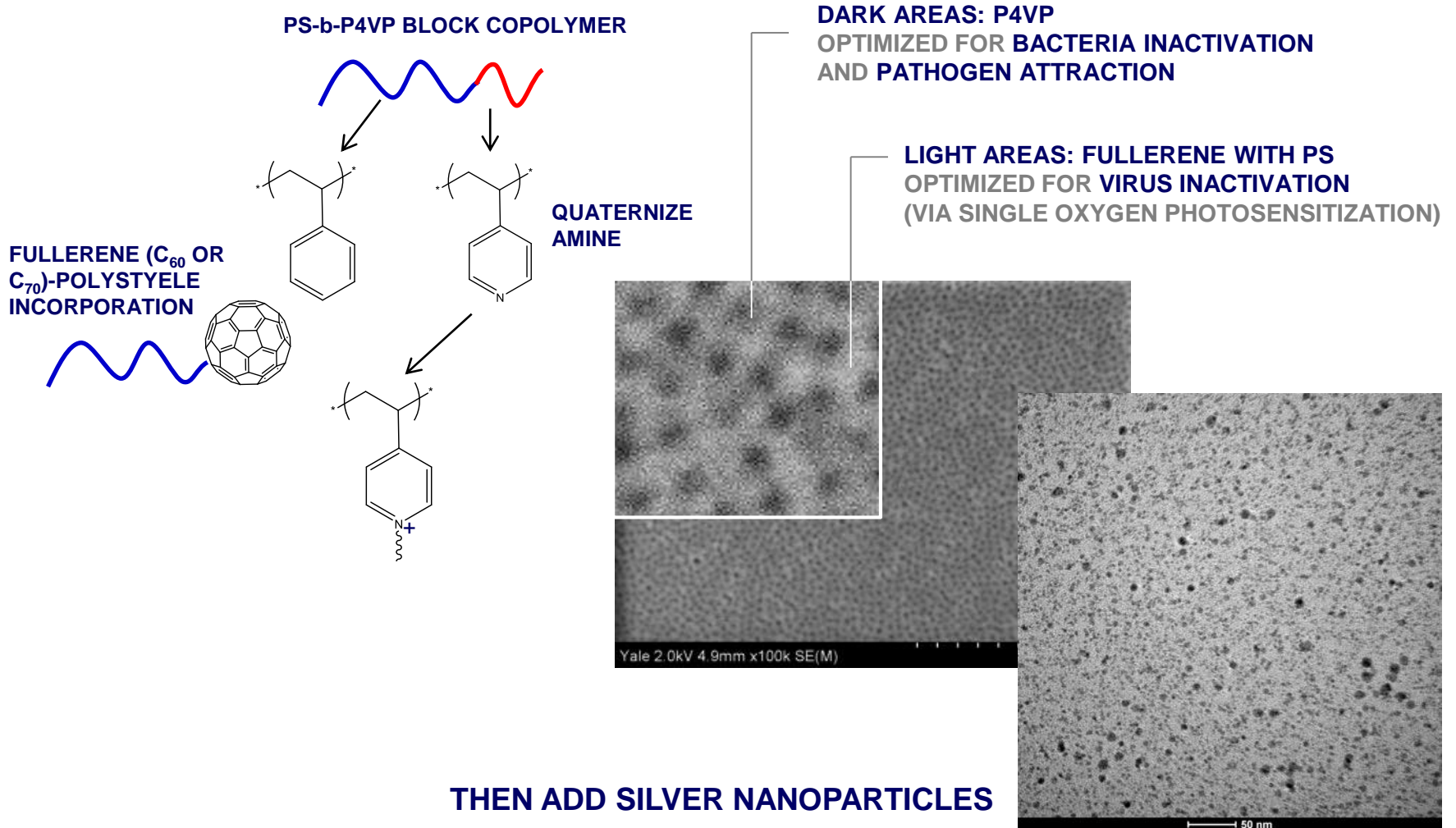
AGGREGATION IS A PREVALENT CONCERN

TOO WIDELY SPACED

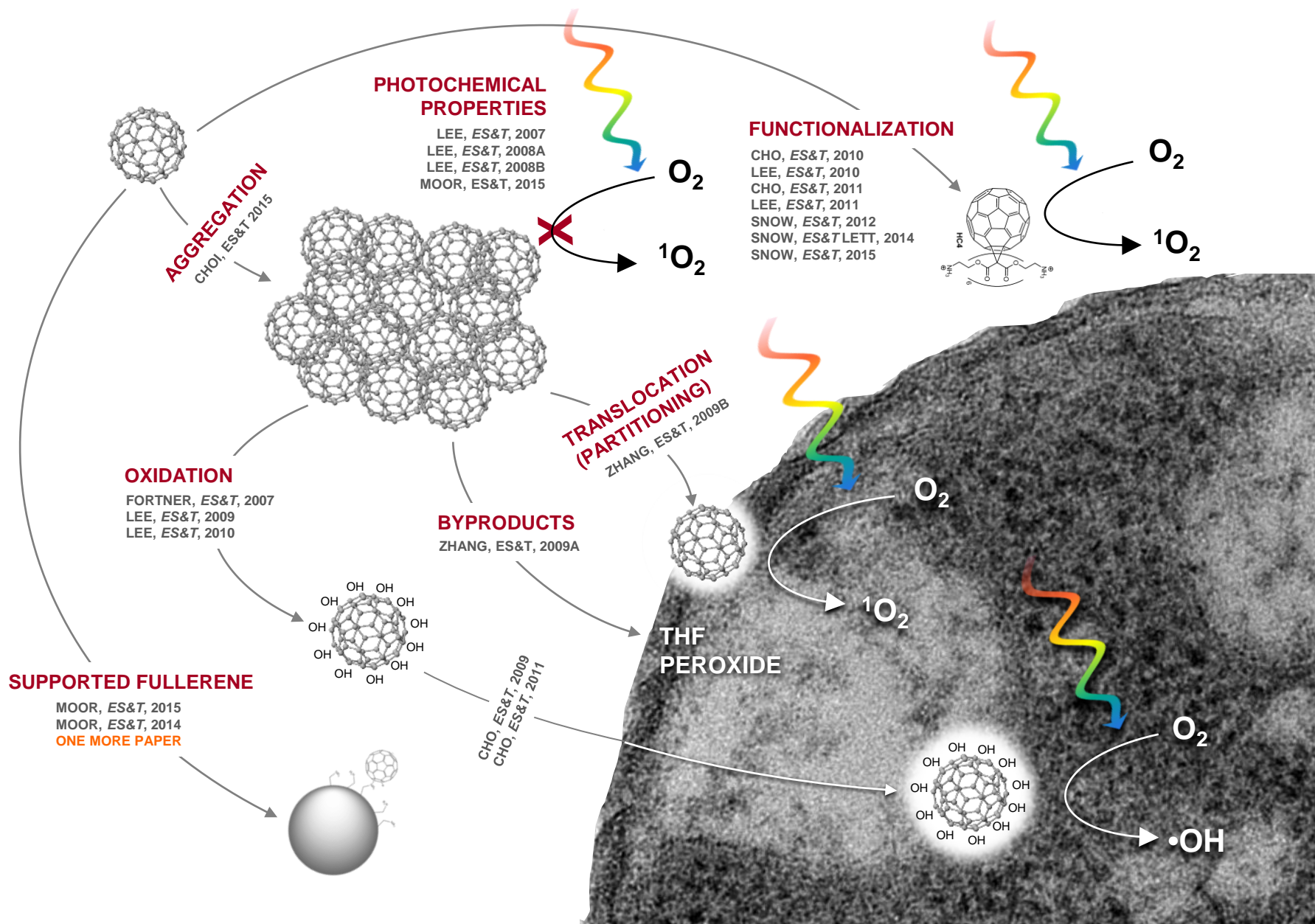
LOW EFFICIENCY

USING **BLOCK-COPOLYMER** TEMPLATE FOR LENGTH SCALE CONTROL

MOOR ET AL., ACS APPL. MATER. INTERFACES, 8(49), 33583-33591



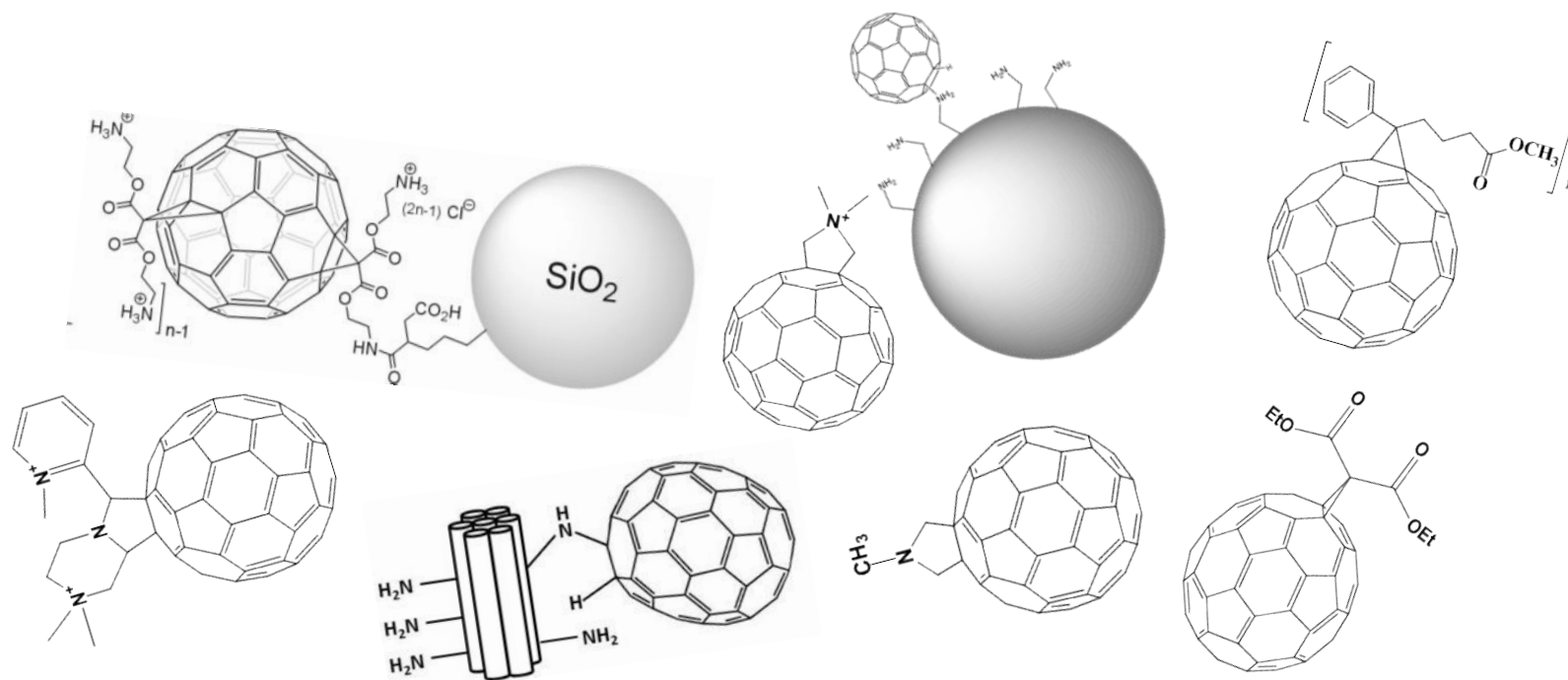
FULLENE: FROM ENVIRONMENTAL IMPLICATION TO DISINFECTION APPLICATION



SOLAR DISINFECTION (SODIS)



IN THE PAST, WE STUDIED PHOTOSENSITIZERS LIKE:



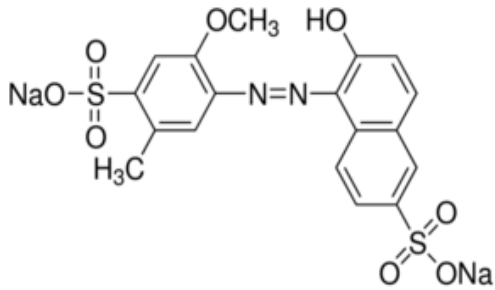
LIKELY REPOSE FROM INDUSTRY:



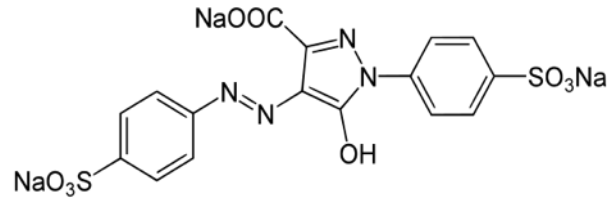
HOW ABOUT SOMETHING EDIBLE?

LIKE SYNTHETIC FOOD DYES

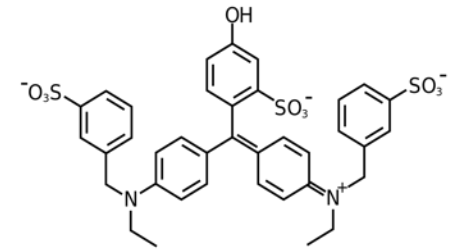
ALLURA RED AC



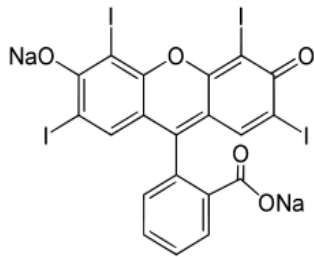
TARTRAZINE



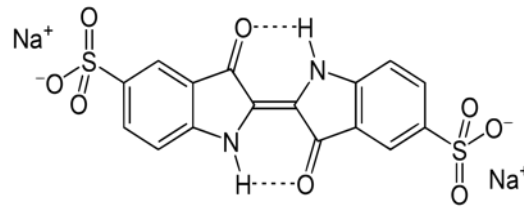
FAST GREEN FCF



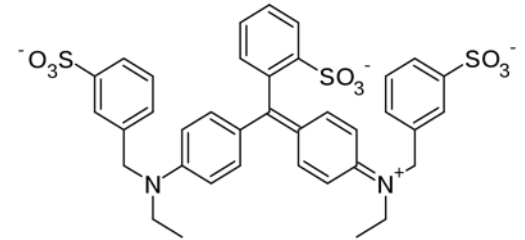
ERYTHROSINE



INDIGO CARMINE

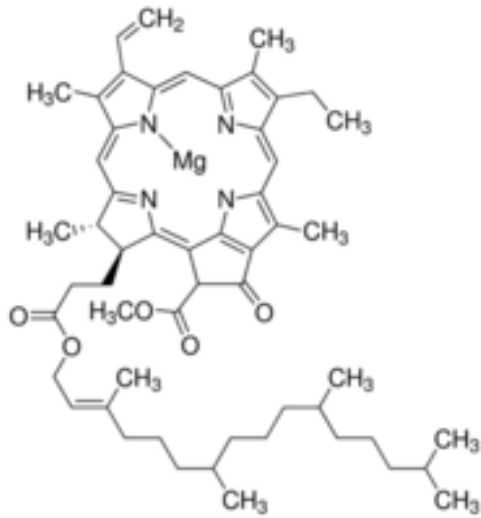


BRILLIANT BLUE FCF

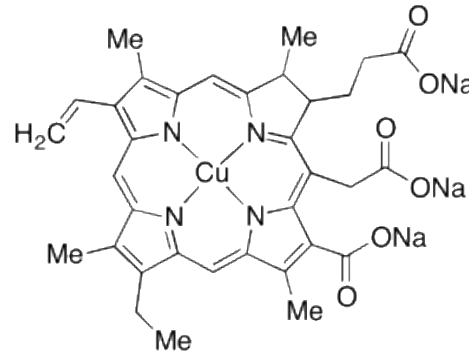


.... APPROVED BY THE FDA!!!

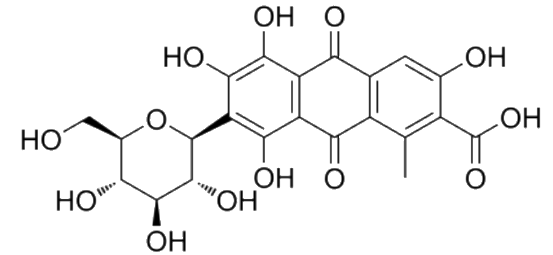
... OR EVEN NATURAL DYES



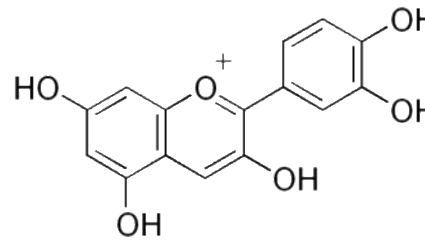
CHLOROPHYLL A



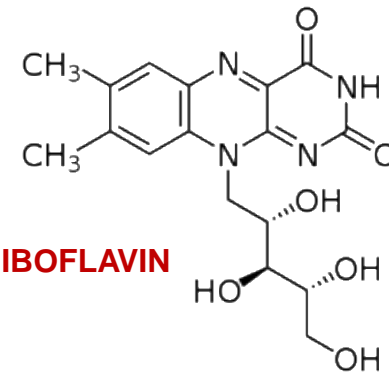
CHLOROPHYLLIN



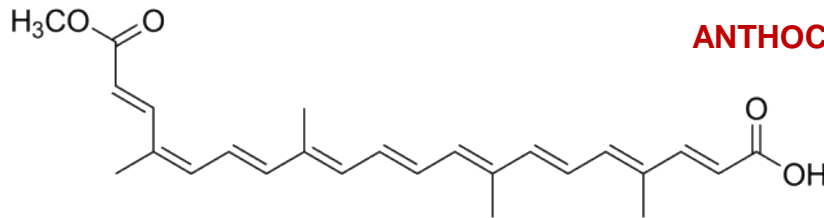
COCHINEAL EXTRACT



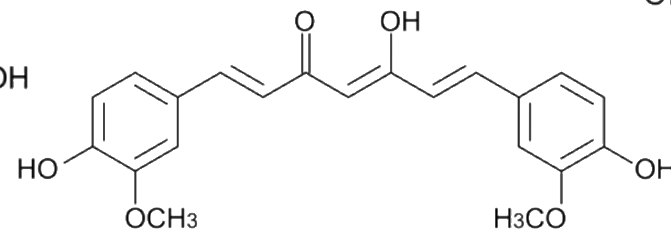
ANTHOCYANINS



RIBOFLAVIN



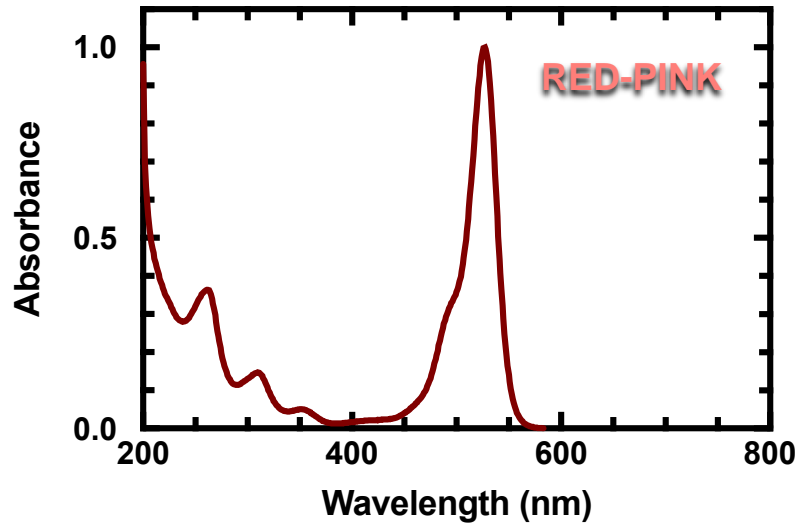
ANNATTO SEED EXTRACT



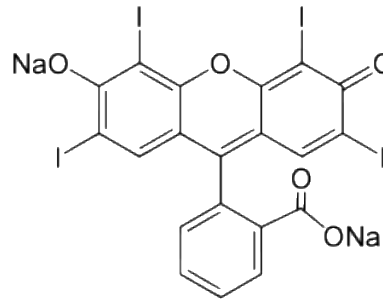
CURCUMIN

TWO PROMISING CANDIDATES

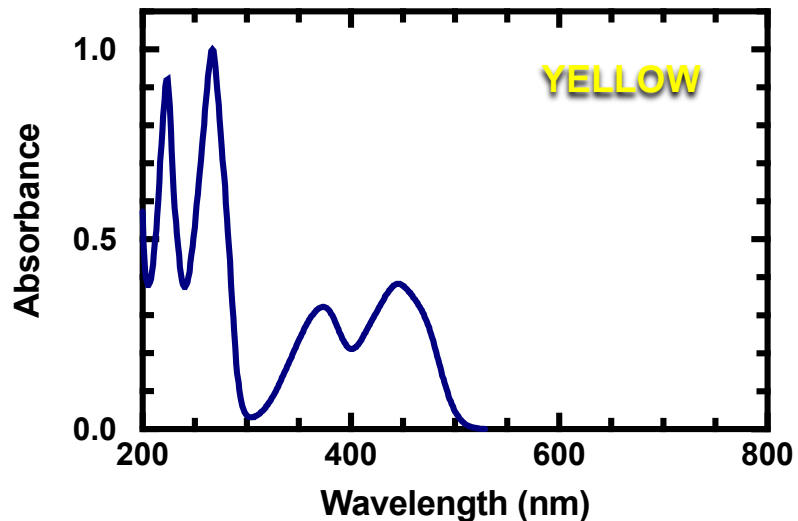
THAT WE FOUND SO FAR



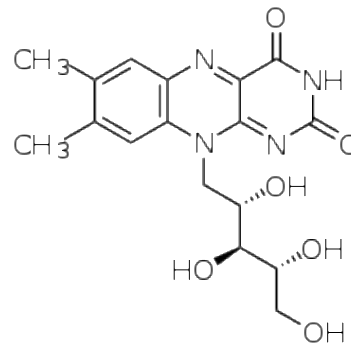
ERYTHROSINE



- FD&C RED NO. 3
- COMMONLY FOUND IN PINK PROCESSED FOODS
- NO OBSERVED ADVERSE EFFECTS AT 60 MG/KG BODYWEIGHT

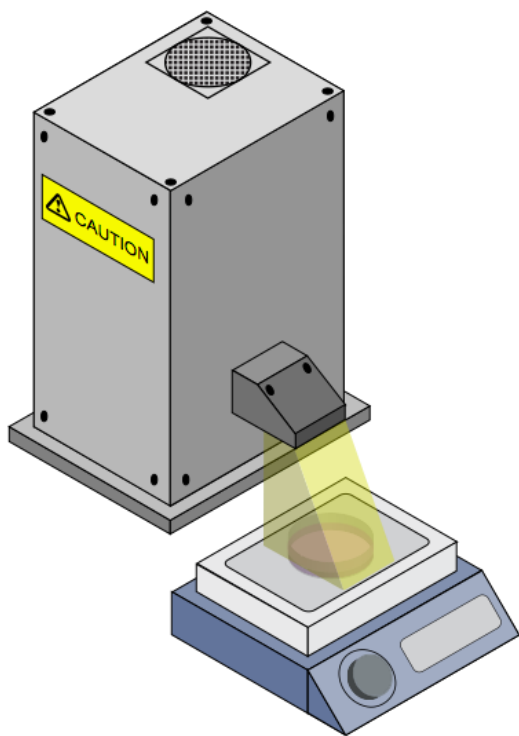


RIBOFLAVIN



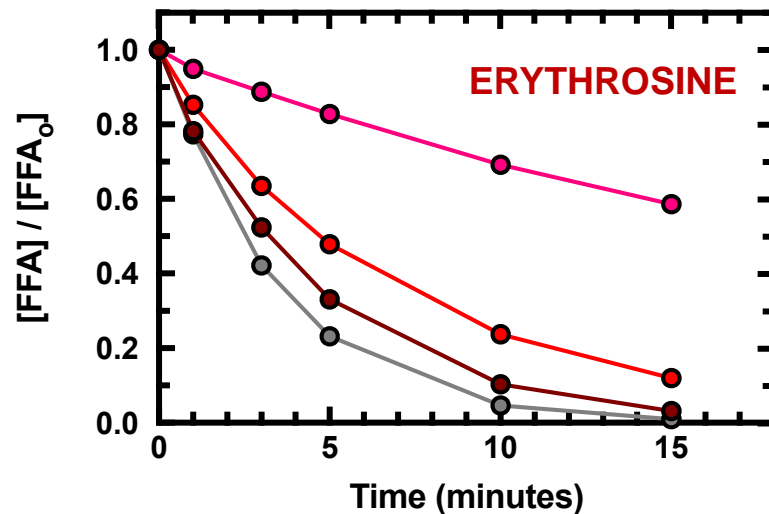
- VITAMIN B2
- USED AS A PHOTSENSITIZER FOR BIOLOGICAL EXPERIMENTS
- NATURALLY OCCURRING MEDICAL DOSES OF 400 MG WITHOUT ADVERSE EFFECTS

BOTH ERYTHROSINE AND RIBOFLAVIN PRODUCE $^1\text{O}_2$



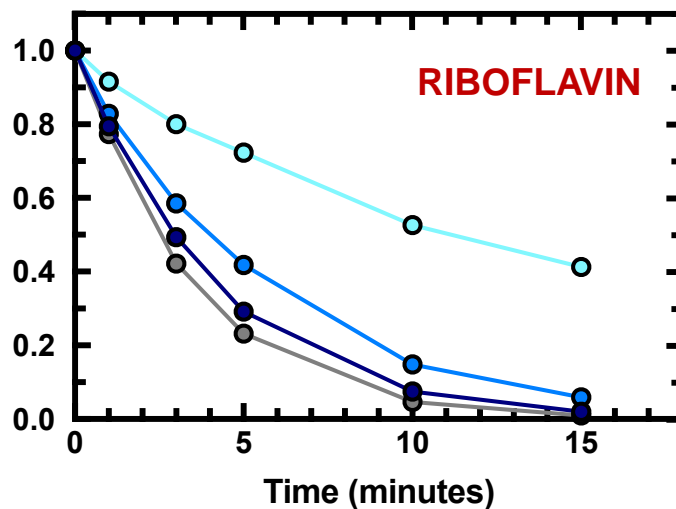
SINGLET
OXYGEN
PROBE

[FFA] / [FFA₀]



**BENCHMARK
PHOTOSENSITIZER**

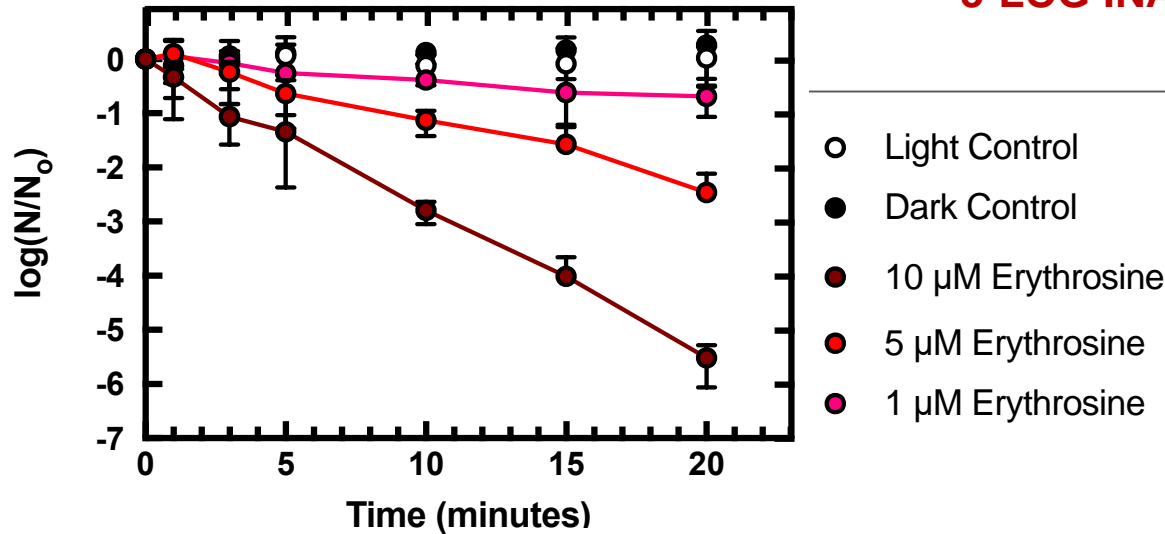
- 10 μM Rose Bengal
- 10 μM Erythrosine
- 5 μM Erythrosine
- 1 μM Erythrosine



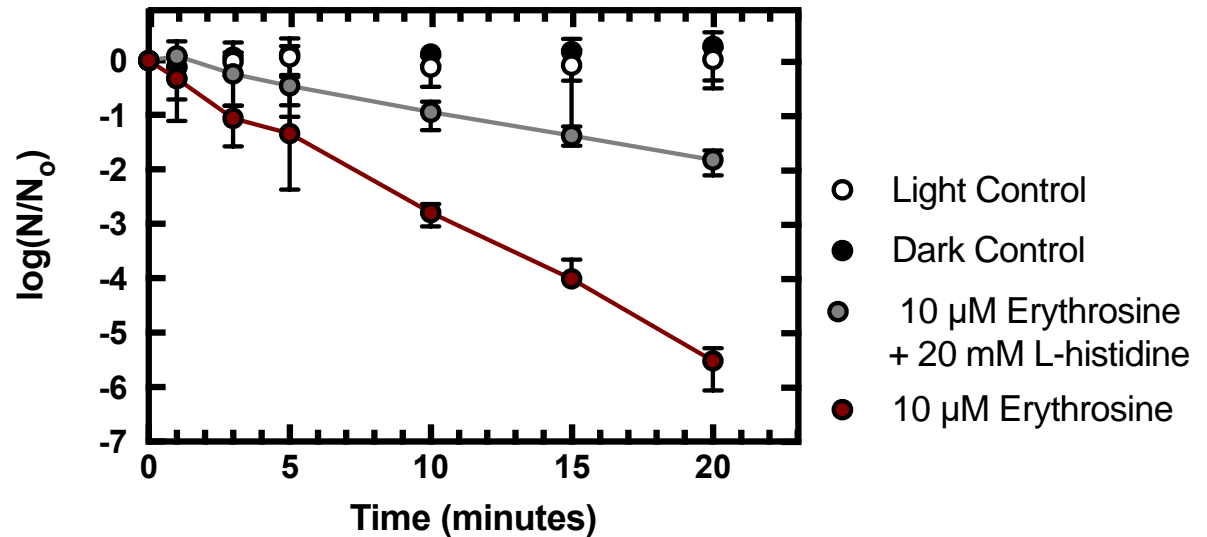
- 10 μM Rose Bengal
- 100 μM Riboflavin
- 50 μM Riboflavin
- 10 μM Riboflavin

ERYTHROSINE KILLS MS2 BACTERIOPHAGE

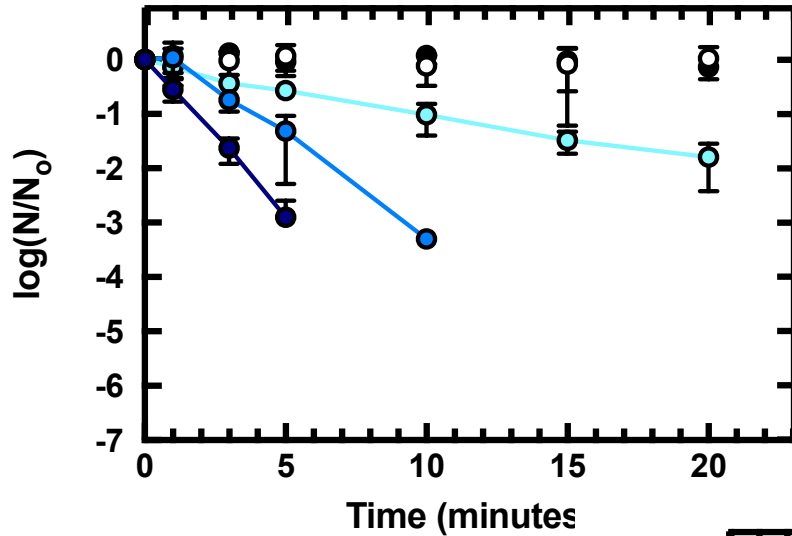
**3-LOG INACTIVATION OBSERVED IN
10 MIN with 10 μM**



$^1\text{O}_2$ IS THE PRIMARY ROS

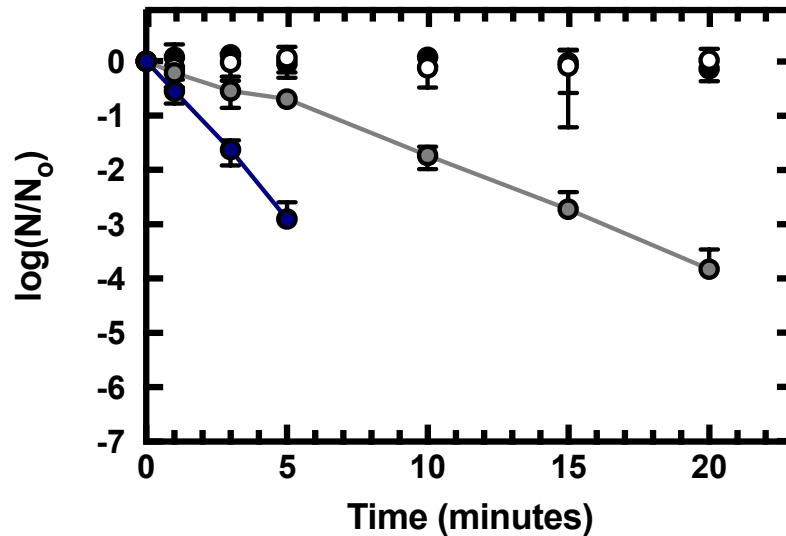


SO DOES RIBOFLAVIN

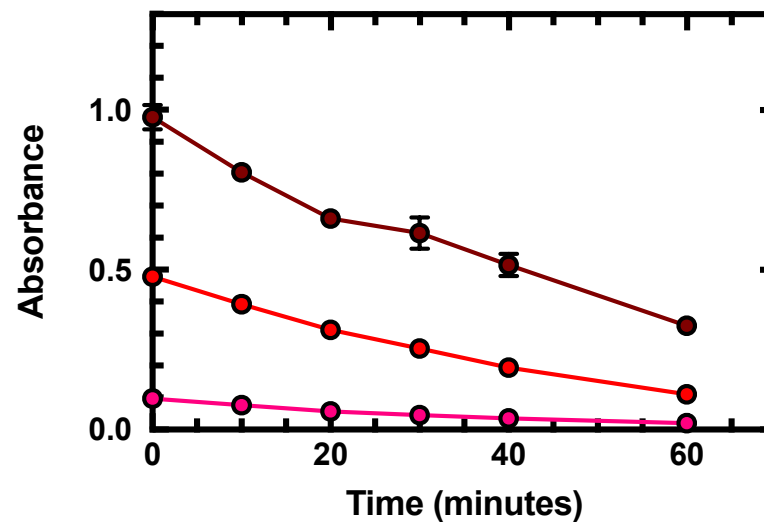
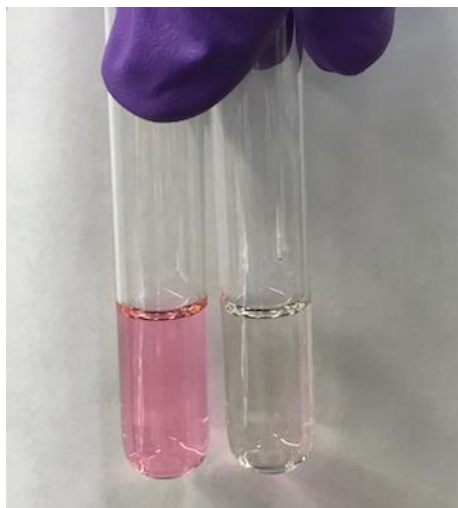


**3-LOG INACTIVATION OBSERVED
IN 5 MIN WITH 100 μM**

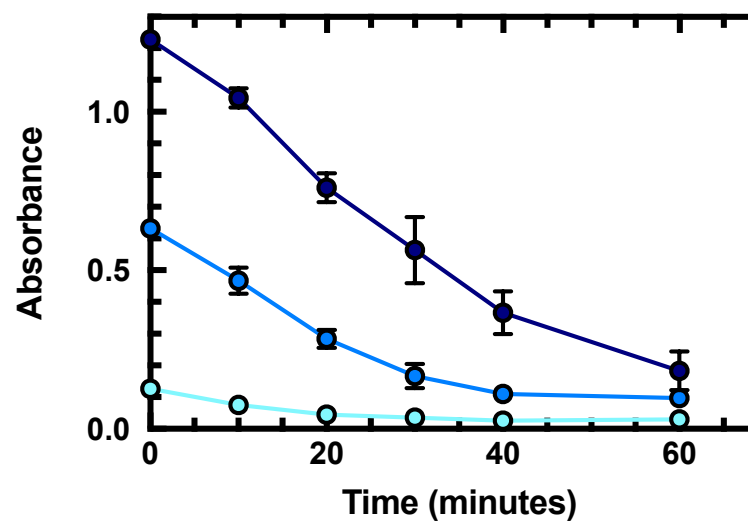
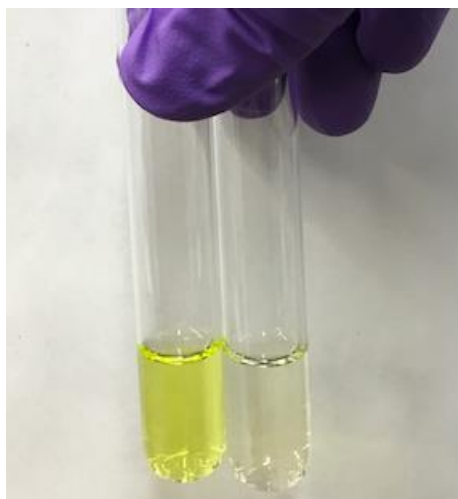
$^1\text{O}_2$ IS THE PRIMARY ROS



AND THEY PHOTBLEACH!!!

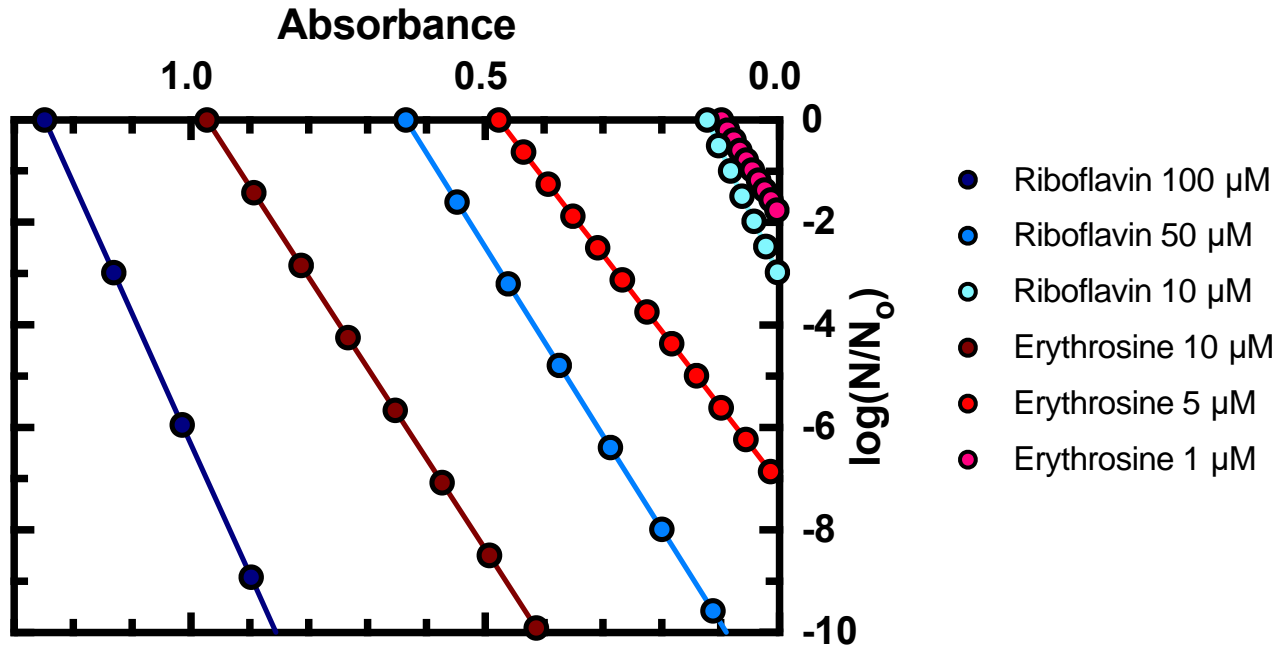


- Erythrosine 10 μM
- Erythrosine 5 μM
- Erythrosine 1 μM



- Riboflavin 100 μM
- Riboflavin 50 μM
- Riboflavin 10 μM

COLOR CHANGE AS AN INDICATOR FOR DISINFECTION EFFECTIVENESS



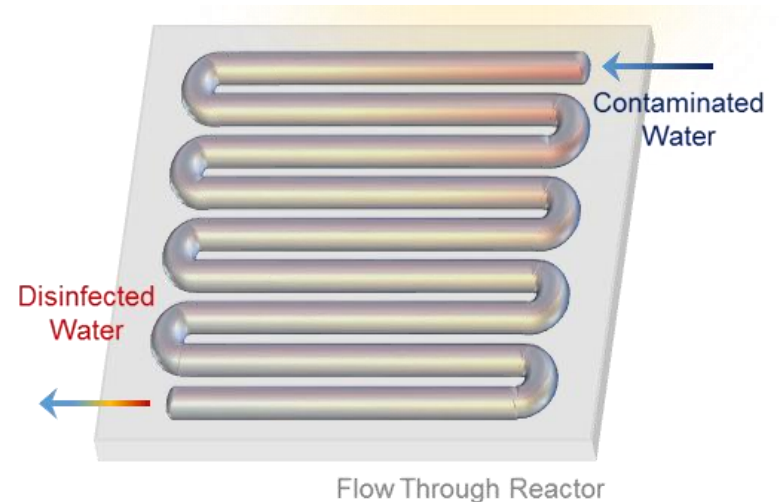
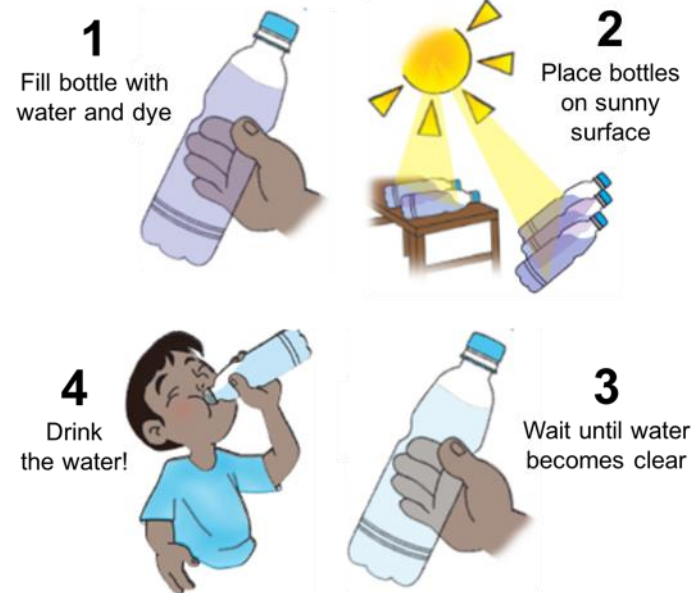
COMPLETE PHOTBLEACHING CORRESPONDS TO GREATER THAN **6-LOG** INACTIVATION FOR 10, 5 μM ERYTHROSINE, AND 100, 50 μM RIBOFLAVIN

CONCLUSIONS SO FAR

ERYTHROSINE, AN FDA APPROVED FOOD DYE, AND **RIBOFLAVIN**, VITAMIN B2, **PRODUCE SINGLET OXYGEN** AND **PHOTBLEACH**

ERYTHROSINE AND RIBOFLAVIN ARE ABLE TO **DEGRADE A VARIETY OF MICROPOLLUTANTS** OF PUBLIC HEALTH INTEREST

FOOD DYES ARE **CAPABLE OF INACTIVATING MS2**, REDUCING THE TIME NEEDED FOR 3-LOG INACTIVATION FROM SEVERAL HOURS TO 5 – 10 MINUTES



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