FULLERENE: FROM ENVIRONMENTAL IMPLICATION TO DISINFECTION APPLICATION …AND BEYOND

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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

\[ E_{\text{formation}} = -2.983 \text{ kcal/mol} \]

\[ E_{\text{formation}} = -2.305 \text{ kcal/mol} \]

INTERACTION OF THE LONE PAIR OF ELECTRONS OF OXYGEN WITH Π*-ORBITALS OF C\textsubscript{60} (RATHER THAN A HYDROGEN BONDING INTERACTION AS IN THE CASE OF BENZENE)

C\textsubscript{60} ACQUIRES A PARTIAL NEGATIVE CHARGE FROM WATER MOLECULE.
HYDROGEN BOND NETWORK OF 10 WATER MOLECULES ON SINGLE C\textsubscript{60}

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

C\textsubscript{60} CAN BE POLARIZED BY WATER MOLECULES, POTENTIALLY ENHANCING THE SOLVATION OF C\textsubscript{60} BY WATER

\begin{align*}
Q(\text{position 1}) &= -0.0492e \\
Q(\text{position 2}) &= -0.0241e \\
Q(\text{position 3}) &= 0.0126e
\end{align*}

MOST (83\%) OF FORMATION ENERGY FOR C\textsubscript{60}-10H\textsubscript{2}O CLUSTER RESULTS FROM INTERACTION AMONG WATER MOLECULES
PRESENCE OF ANOTHER C\textsubscript{60} HAS NEGLIGIBLE EFFECT ON THE HYDROGEN BONDING NETWORK FORMATION AND THE CHARGE TRANSFER FROM WATER MOLECULES TO C\textsubscript{60}.

THIS POLARIZATION OF THE TWO C\textsubscript{60}S LIKELY ENHANCES THE STRENGTH OF THE C\textsubscript{60}-C\textsubscript{60} INTERACTION VIA ELECTROSTATIC ATTRACTION BETWEEN OPPOSITE CHARGES.
'O₂ CLAIMED TO BE RESPONSIBLE FOR CELL “DEATH”

IS THAT TRUE?
C\textsubscript{60} AGGREGATES ARE NOT VERY PHOTOACTIVE

Lee et al., Environ. Sci. Technol., 2007, 41, 2529-2535
Lee et al., Environ. Sci. Technol., 2008, 42, 3459-3464

PHOTOCHEMICAL PROPERTY CHANGES A LOT DEПENDING ON AQUEOUS DISPERSION STATE

NANO-SECOND LASER FLASH PHOTOLYSIS

FEMTO-SECOND LASER FLASH PHOTOLYSIS
Perhaps there is a way for C$_{60}$ to get into cells in molecular form?

...or something other than C$_{60}$ is involved in cell toxicity?
C$_{60}$ IN C$_{60}$ AGGREGATES CAN MOVE INTO MICELLES


Some other pieces of evidence:

- Change in UV-Vis absorption spectra
- Change in surfactant micelle fluorescence spectra
- Particle stability (with MgClO$_4$ addition)
- TEM image analysis

C$_{60}$ in C$_{60}$ aggregates can move into micelles under UVA irradiation. Translocation into the micelle core leads to no $^{1}$O$_2$ production. With MgClO$_4$ addition, $^{1}$O$_2$ is produced.
THERE IS SOMETHING SMELLY IN THE SOUP

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

THF/nC$_{60}$ HAS BEEN CONSISTENTLY REPORTED TO BE MORE TOXIC THAN OTHER FORMS OF nC$_{60}$

E. COLI INACTIVATION WAS MOSTLY DUE TO THF PEROXIDE
FULLEROL KNOWN TO BE MORE TOXIC

CAN COMMON OXIDANTS OXYDIZE nC₆₀?
WHAT ARE THE PRODUCTS?
HOW DO PRODUCTS BEHAVE?
nC₆₀ IN WATER CAN BE OXIDIZED BY O₃, 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
WHAT UNIQUE PROPERTIES DO OTHER FUNCTIONALIZED C_{60}S HAVE?

**Aggregation**
- LEE, ES&T, 2007
- LEE, ES&T, 2008A
- LEE, ES&T, 2008B
- MOOR, ES&T, 2015

**Oxidation**
- FORTNER, ES&T, 2007
- LEE, ES&T, 2009
- LEE, ES&T, 2010

**Byproducts**
- ZHANG, ES&T, 2009A
- ZHANG, ES&T, 2009B

**Photochemical Properties**
- ZHANG, ES&T, 2009

**Thf Peroxide**

\[ \text{THF Peroxide} \]

\[ \text{\textbullet OH} \]

\[ \text{\textbullet OH} \]
AMINE-FUNCTIONALIZED C$_{60}$ 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

EXPERIMENTS PERFORMED UNDER ATLANTA SUNLIGHT

$^{1}\text{O}_2$ KILLS VIRUS IN WATER

CUSTOM-DERIVATIZED C$_{60}$ TAKES SUNLIGHT IN BOTH UV AND VIS

$^{1}\text{O}_2$ $\text{O}_2$
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.

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

THIS STUDY

PREVIOUS STUDIES
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

INITIAL DISTANCE = 1.3 nm

SIGNIFICANTLY WEAKER INTERACTIONS BETWEEN B SERIES FULLERENES
FULLERENE-WATER INTERACTION

RAMAN SPECTROSCOPY

O-H SYMMETRIC BENDING

- DI Water
- nC60
- A2
- A3
- B2
- B3

MORE STRUCTURED HYDRATION ENVIRONMENT

RADIAL DISTRIBUTION FUNCTION

1\textsuperscript{ST} HYDRATION SHELL = 6.5 Å

2\textsuperscript{ND} HYDRATION SHELL = 9.5 Å

DECREASING WATER DENSITY
FULLERENE-OXYGEN INTERACTION
INTERACTION ENERGIES

Intensity (black: nm, red kcal/mol)

-2  -1  0  1  2

Distance
Interaction Energy

Time (ns)

0.0  0.2  0.4  0.6  0.8  1.0

C_{60}

A2

B2

Distance
Interaction Energy

Time (ns)

0.0  0.2  0.4  0.6  0.8  1.0
PHOTOCHEMICAL PROPERTIES
LEE, ES&T, 2007
LEE, ES&T, 2008A
LEE, ES&T, 2008B
MOOR, ES&T, 2015

FUNCTIONALIZATION
CHO, ES&T, 2010
LEE, ES&T, 2010
LEE, ES&T, 2011
SNOW, ES&T, 2012
SNOW, ES&T LETT, 2014
SNOW, ES&T, 2015

OXIDATION
FORTNER, ES&T, 2007
LEE, ES&T, 2009
LEE, ES&T, 2010

BYPRODUCTS
ZHANG, ES&T, 2009A
ZHANG, ES&T, 2009B

TRANSLOCATION (PARTITIONING)
ZHANG, ES&T, 2009B

LEET’S TRY SOME MORE DISINFECTION APPLICATION

THF PEROXIDE

•OH
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

MORE SURFACE AREA
USING MCM41

MORE PHOTOACTIVITY
USING C_{70}
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

PS-b-P4VP BLOCK COPOLYMER

FULLERENE (C_{60} OR C_{70})-POLYSTYRENE INCORPORATION

QUATERNIZE AMINE

DARK AREAS: P4VP OPTIMIZED FOR BACTERIA INACTIVATION AND PATHOGEN ATTRACTION

LIGHT AREAS: FULLERENE WITH PS OPTIMIZED FOR VIRUS INACTIVATION (VIA SINGLE OXYGEN PHOTOSENSITIZATION)

THEN ADD SILVER NANOPARTICLES
FULLERENE: FROM ENVIRONMENTAL IMPLICATION TO DISINFECTION APPLICATION

PHOTOCHEMICAL PROPERTIES
LEE, ES&T, 2007
LEE, ES&T, 2008A
LEE, ES&T, 2008B
MOOR, ES&T, 2015

FUNCTIONALIZATION
CHO, ES&T, 2010
LEE, ES&T, 2010
CHO, ES&T, 2011
LEE, ES&T, 2011
SNOW, ES&T, 2012
SNOW, ES&T LETT, 2014
SNOW, ES&T, 2015

AGGREGATION
LEE, ES&T, 2015

OXIDATION
FORTNER, ES&T, 2007
LEE, ES&T, 2009
LEE, ES&T, 2010

BYPRODUCTS
ZHANG, ES&T, 2009A

TRANSLOCATION (PARTITIONING)
ZHANG, ES&T, 2009B

SUPPORTED FULLERENE
MOOR, ES&T, 2015
MOOR, ES&T, 2014
ONE MORE PAPER

THF PEROXIDE

•OH

1O2

O2

Lee, ES&T, 2007
Lee, ES&T, 2008A
Lee, ES&T, 2008B
Moor, ES&T, 2015

Lee, ES&T, 2010
Lee, ES&T, 2010
Lee, ES&T, 2011
Snow, ES&T, 2012
Snow, ES&T LETT, 2014
Snow, ES&T, 2015

Fortner, ES&T, 2007
Lee, ES&T, 2009
Lee, ES&T, 2010

Moor, ES&T, 2015
Moor, ES&T, 2014
One More Paper

Supported Fullerene

Oxidation
Fortner, ES&T, 2007
Lee, ES&T, 2009
Lee, ES&T, 2010

Byproducts
Zhang, ES&T, 2009A

Translocation (Partitioning)
Zhang, ES&T, 2009B

Moor, ES&T, 2015
Moor, ES&T, 2014
One More Paper

Photochemical Properties
Lee, ES&T, 2007
Lee, ES&T, 2008A
Lee, ES&T, 2008B
Moor, ES&T, 2015

Fullerene: From Environmental Implication to Disinfection Application
SOLAR DISINFECTION (SODIS)
IN THE PAST, WE STUDIED PHOTOSENSITIZERS LIKE:

LIKELY RESPONSE FROM INDUSTRY:
HOW ABOUT SOMETHING EDIBLE?
LIKE SYNTHETIC FOOD DYES

ALLURA RED AC

ERYTHROSINE

TARTRAZINE

INDIGO CARMINE

FAST GREEN FCF

BRILLIANT BLUE FCF

.... APPROVED BY THE FDA!!!
… OR EVEN NATURAL DYES

- CHLOROPHYLLIN
- COCHINEAL EXTRACT
- RIBOFLAVIN
- ANTHOCYANINS
- ANNATTO SEED EXTRACT
- CURCUMIN
TWO PROMISING CANDIDATES
THAT WE FOUND SO FAR

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

- VITAMIN B2
- USED AS A PHOTOSENSITIZER FOR BIOLOGICAL EXPERIMENTS
- NATURALLY OCCURRING MEDICAL DOSES OF 400 MG WITHOUT ADVERSE EFFECTS
BOTH ERYTHROSINE AND RIBOFLAVIN PRODUCE $^1O_2$

**Graphs:**

- **ERYTHROSINE**
  - [FFA] / [FFA_o]
  - Time (minutes)
  - 10 µM Rose Bengal
  - 10 µM Erythrosine
  - 5 µM Erythrosine
  - 1 µM Erythrosine

- **RIBOFLAVIN**
  - [FFA] / [FFA_o]
  - Time (minutes)
  - 10 µM Rose Bengal
  - 100 µM Riboflavin
  - 50 µM Riboflavin
  - 10 µM Riboflavin

**Legend:**
- BENCHMARK PHOTOSENSITIZER
- 10 µM Rose Bengal
- 10 µM Erythrosine
- 5 µM Erythrosine
- 1 µM Erythrosine
- 100 µM Riboflavin
- 50 µM Riboflavin
- 10 µM Riboflavin
ERYTHROSOINE KILLS MS2 BACTERIOPHAGE

3-LOG INACTIVATION OBSERVED IN 10 MIN with 10 µM

1O₂ IS THE PRIMARY ROS
SO DOES RIBOFLAVIN

3-LOG INACTIVATION OBSERVED IN 5 MIN WITH 100 µM

1O₂ IS THE PRIMARY ROS
AND THEY PHOTOBLEACH!!!
COLOR CHANGE AS AN INDICATOR
FOR DISINFECTION EFFECTIVENESS

COMPLETE PHOTOBLEACHING 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 PHOTobleach

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
THANKS TO

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