Light-Initiated Transformation of C_{60} Cluster in Water

Lingjun (Lynn) Kong[1], Yau Fong (Kyle) Chan[2], Richard G. Zepp[3], Cissy Ma[3], Dermont Bouchard[3], and Carl Isaacson[1]

[1]National Research Council Associate, US Environmental Protection Agency, NERL/ERD, Athens GA, 30605; [2]Student Service Associate, Ecosystems Research Division, US EPA, Athens GA, 30605; [3]US EPA, NERL/ERD, Athens GA, 30605

Abstract

Although Buckminster fullerene (C_{60}) has an extremely low water solubility (~8 ng/L), the formation of stable clusters (aqu/nC_{60}) not only greatly increases the mass of C_{60} dispersed in water, but also alters its physicochemical properties. This research focused on investigating the light-initiated transformation processes of aqu/nC_{60} aggregates in water. The irradiation kinetics of aqu/nC_{60} with simulated solar and monochromatic irradiation were investigated. The direct photoreaction of aqu/nC_{60} exhibited first-order kinetics with reaction quantum yields of 1.48 (± 0.05) × 10^{-5} and 1.46 (± 0.06) × 10^{-5} at 366 and 435 nm, respectively. Following irradiation by simulated solar radiation the fluorescence EEMs of the aqueous phase of aqu/nC_{60} extracted with toluene showed an initial increase (7 days) and an ultimate decrease (12 days) with the emission peak shifted to a shorter wavelength. This result displays the same pattern observed with fullerenol, a hydroxylated C_{60}, under simulated solar irradiation, suggesting that the photolysis of aqu/nC_{60} leads to formation of hydrophilic functional groups (i.e. -OH or -C=O, etc). MALDI-TOF-TOF MS of both the toluene and water phase of C_{60} extracted with toluene also implies the possible formation of more hydrophilic products following irradiation.

Experimental

- C_{60} (99%, MER Corp., Tuscon, AZ)
- Irradiation kinetic studies (22°C):
  - Full spectrum irradiation: Atlas SunTest CPS solar simulator, 1 kW Xenon lamp (Atlas)
  - Monochromatic irradiation: Merry-go-round reactor (MGRR), mercury vapor lamp; glass filters isolating 366 nm light
- Fluorescence:
  - ISA-APEX Jobin Yvon Fluorolog 3-12 scanning fluorometer
- Mass spectroscopy:
  - 4700 Proteomics Analyzer

Results

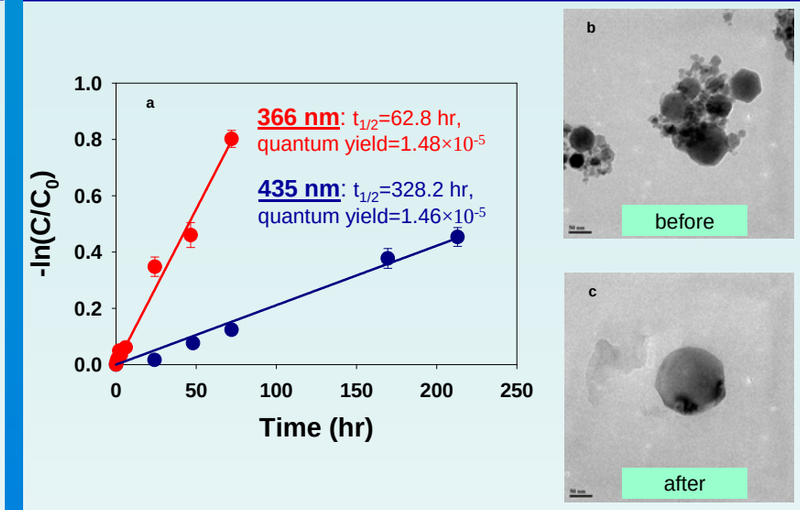

Figure 1. **(a)** Aqu/C_{60} degradation kinetics in MGRR at 366 and 435 nm. Light intensity were 0.00724 and 0.00190 einstein L^{-1} h^{-1} at 366 and 435, respectively. **(b)** and **(c)** are representative TEMs of C_{60} clusters before and after exposure to simulated solar light, respectively.

a) EEM of fullerenol aqueous solution

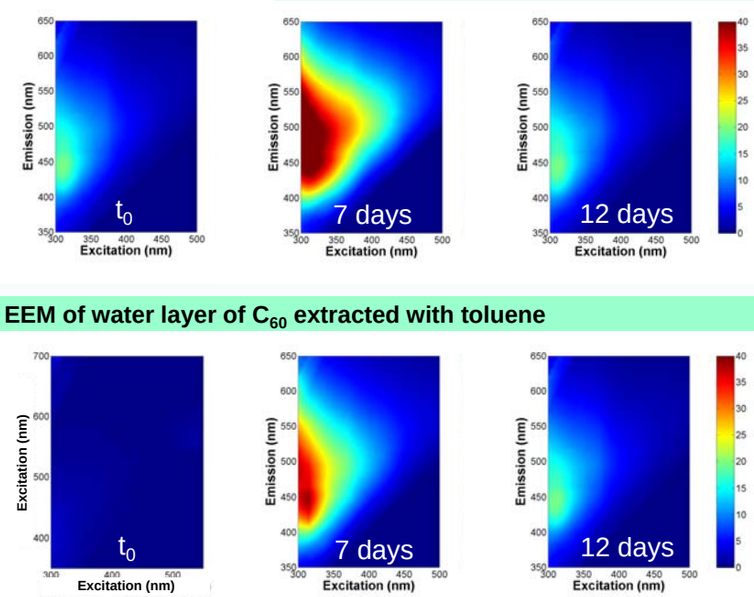

Figure 2. Comparison of Excitation-Emission Matrix scan (EEM) of C_{60} and fullerenol. An initial increase (7 days) and an ultimate decrease (12 days) with the emission peak shifted to a shorter wavelength

Results (Continued)

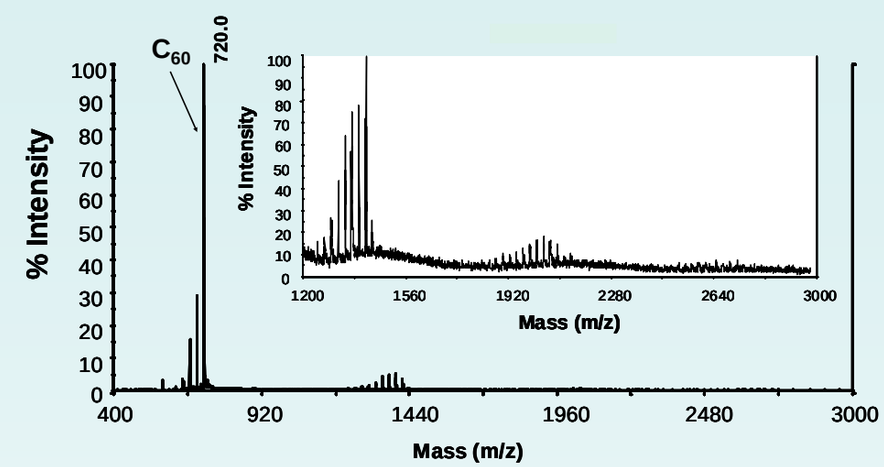

Figure 3. MALDI-TOF-TOF mass spectrometry of the water layer of irradiated C_{60} extracted with toluene.

The parent C_{60} peak at 720 m/z as well as the 696, 672, and 648 m/z peaks were found in both non-irradiated and irradiated samples, indicating the peaks of less of 2 C (696 m/z), 4 C (672 m/z) and 6 C (648 m/z) were caused by the fragmentation during the ionization. However the dimmer and trimmer peaks were only observed in the toluene layer of non-irradiated C_{60} and the water layer of irradiated C_{60} extracted with toluene.

Conclusions

- C_{60} aggregates in water are photoreactive and photodegradation kinetics are first-order; the half life ($t_{1/2}$) are 62.8 and 328.2 hrs at 366 and 435 nm, respectively. However, the reaction quantum yields (Φ_λ) are comparable, with values of 1.48 (± 0.05) × 10^{-5} and 1.46 (± 0.06) × 10^{-5}, respectively.
- The EEMs of the aqueous phase of aqu/nC_{60} (extracted with toluene) following simulated solar irradiation display the same pattern as that of aqueous fullerenol under the same irradiation, suggesting that the photolysis of aqu/nC_{60} leads to formation of hydrophilic functional groups (i.e. -OH or -C=O, etc).
- MALDI-TOF-TOF mass spectrometry doesn't give a complete identification of the photoproducts of C_{60}, which is most likely due to the facile fragmentation of these products. However, the MS results indicate the formation of more hydrophilic products following irradiation.

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