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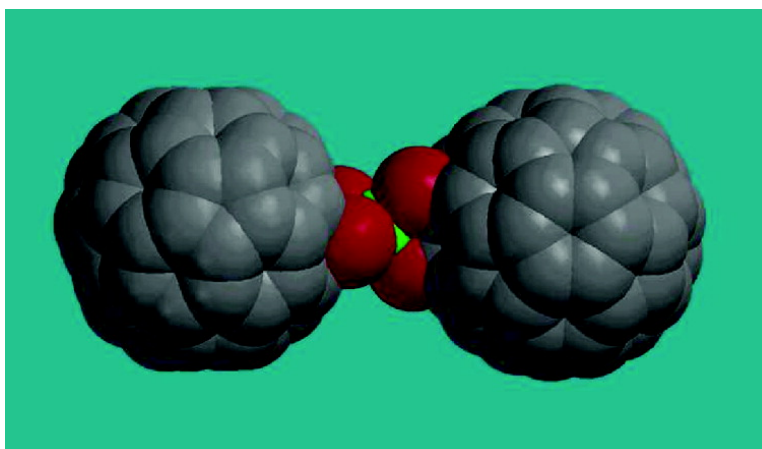
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# Reaction of Hydroxyfullerene with Metal Salts: A Route to Remediation and Immobilization

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There has recently been much publicity given to both the potential toxicity[1] and physiological benefit[2] of fullerenes and their derivatives. With regard to toxicity, interest has focused on the water-soluble aggregate $n$-$C_{60}$ formed by either the partial hydrolysis of $C_{60}$ or the water extraction of a $C_{60}$-solvent clathrate from organic solvents.[3] Studies with human skin (HDF) and liver carcinoma (HepG2) cells[4] and large mouth bass[5] have indicated potential concerns that $n$-$C_{60}$ shows a high toxicity. In contrast, hydroxy-fullerenes [fullerenol, "$C_{60}(OH)_n$"][6] were shown to have negligible toxicity.[5,7] On the basis of this observation, a pathway to environmental remediation of fullerenes can be envisaged based upon an oxidation/hydrolysis protocol. However, it is appreciated that toxicity is just one issue that must be considered with regard to the environmental impact of nanoparticles. The transport of the nanomaterials in the environment is also of great importance. In this regard, Wiesner and co-workers[8] have reported that $n$-$C_{60}$ has a very low mobility in aqueous solution through a porous medium (the lowest mobility of the inorganic material investigated in the study); conversely, hydroxyfullerenes are very mobile. Thus the fullerene material with the lowest observed toxicity would appear to have the highest mobility in aqueous environments, and that with the highest toxicity the least mobile.[8] Despite the apparent low toxicity of $C_{60}(OH)_n$, there are still concerns that its ease of transport may allow accumulation in the environment. We report herein that hydroxyfullerene reacts rapidly and irreversibly (across a wide pH range) with a variety of metal salts under ambient aqueous conditions to produce insoluble metal–hydroxyfullerene cross-linked polymers (M–fullerenol), thus providing a limit to the mobility in an aquatic environment.

In a typical reaction, the addition of an aqueous solution of $Fe(NO_3)_3$ (0.5 M) to a homogeneous solution of $C_{60}(OH)_n$ (46 mM)[6] results in the precipitation within 1 min of all the fullerenol [as confirmed by UV–visible spectroscopy from the loss of the peak at 220 nm due to $C_{60}(OH)_n$] and the formation of a metal–fullerenol complex. UV–visible spectroscopy indicates that unreacted $Fe^{3+}$ is the predominant species in solution. The use of an excess of the fullerenol results in removal of the metal ion from solution. As may be expected, the rate of the precipitation reaction is proportional to the concentration of both reagents (see Table 1). The formation of the cross-linked material is irreversible across a wide pH range. For example, no $Fe^{3+}$ is liberated from Fe–fullerenol within the pH range of 3.0–8.5. In addition to $H_2O$, the aggregates are insoluble in acetone, $CHCl_3$, toluene, $Et_2O$, and EtOH and decompose in the presence of EDTA.

Similar precipitation events are observed with other metal salts. Aqueous solutions (0.5 M) of $Al(NO_3)_3$, $CaCl_2$, $CoCl_2$, $CuCl_2$, $KMnO_4$, $Ag(NO_3)$, and $ZnCl_2$ were individually reacted with a 4.6 mM aqueous solution of $C_{60}(OH)_n$. In each case, complete precipitation occurred within 1 h. The relative reactivity of the metals salts may be determined by competitive binding reactions.

***Table 1.*** Dependence of Precipitation Time on Reagent Concentration

| [Fe(NO₃)₃] (mM) | [C₆₀(OH)ₙ] (mM) | time to precipitation (min) |
|---|---|---|
| 500 | 46 | <1 |
| 50 | 4.6 | 5 |
| 5 | 0.46 | 85 |
| 0.5 | 0.5 | 720 |
| 0.1 | 0.5 | 4320 |

For example, the use of an equimolar (5 mM) solution of $Fe(NO_3)_3$ and $CoCl_2$ results in the preferential reaction with $Co^{2+}$. Using this approach, a general order of sequestering ability may be determined: Co > Cu > Fe > Al. Wilker and co-workers have shown that for the cross-linking of marine mussel adhesive proteins (containing 3,4-dihydroxyphenylalanine) the effectiveness of cross-linking is heightened by the use of oxidizing metal ions ($MnO4^-$ and $Fe^{3+}$).[9] However, in the present case, while oxidizing species are active, so are nonredox metals, such as $Zn^{2+}$, $Al^{3+}$, and $Ca^{2+}$, suggesting that the fullerenol acts as a chelate ligand to the metal ions.[10]

The precipitate particles vary in size and appearance depending on the metal and the concentration of reactants. SEM images of the agglomerates formed between $Fe^{3+}$ and $C_{60}(OH)_n$ are shown to consist of a textured unstructured material. Similarly, TEM images of samples removed from the reaction mixture prior to precipitation show large particles (100–250 nm) with no observable ordered lattice. AFM images of cross-linked product spin coated on mica show large textured aggregates (0.7–1.1 $\mu$m) comprising of features 1.0–2.7 nm in height.[11]

The XPS of all samples shows the presence of both the appropriate metal and fullerene-like carbon. The M:C ratio is consistent with ca. 2 metals per $C_{60}$ unit. In addition to the presence of the appropriate metal, the O 1s peak shows a significant change in chemical speciation (Figure 1), consistent with the formation of alkoxide versus hydroxide oxygens. Raman and IR spectra do not show bands that are readily assignable; however, the solid-state UV–visible spectrum of the $Fe^{3+}$–fullerenol complex shows, in addition to a band at 270 nm characteristic with fullerenol (282 nm), a shoulder at ca. 340 nm associated with the metal center.

On the basis of the foregoing, we propose that the fullerenol is acting as a chelate ligand to the metals in an analogous manner to the metal cross-linking of marine mussel adhesives.[9] Molecular mechanics calculations[12] on the model systems, $[Fe(C_{60}O_2)_2]$ and $[Fe(C_{60}O_2)_3]$, show that both tetrahedral and octahedral coordination are possible (Figure 2). The lack of ordered structure (observed by TEM and AFM) is expected given the variation of possible isomers (and species) in samples of fullerenol.[13] The resulting material is undoubtedly a random cross-linked polymer. We are continuing our studies on these materials, as well as the characterization of potential model systems.
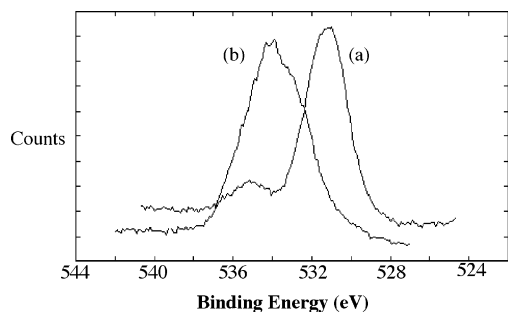
**Figure 1.** The O 1s X-ray photoelectron spectral component of (a) fullerenol and (b) the product from the reaction of $Fe(NO_3)_3$ and $C_{60}(OH)_n$.
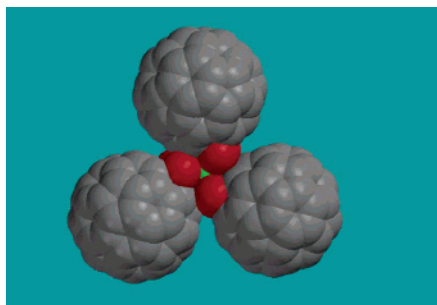


**Figure 2.** Computer-generated structures of a model $[Fe(C_{60}O_2)_3]$ unit, showing the steric accessibility of the cross-linked unit. Carbon (grey), oxygen (red), and iron (green).

Given the presence in the watershed of many of the metals that are found to cross-link fullerenols, it appears that their release into the environment would result in their conversion from soluble, mobile, compounds into insoluble aggregated particles.[14] Furthermore, the presence of metal salts in vivo raises the question as to the potential fate of hydroxyfullerene species. To begin to understand the applicability of these cross-linked aggregates to real systems, we have investigated at what rate would an effluent stream containing fullerenol precipitate given the exposure to environmentally acceptable levels of a metal, such as iron.

The National Pollutant Discharge Elimination System (NPDES) guidelines require a maximum daily concentration of 6 mg·L$^{-1}$ (0.1 mM) with a maximum daily concentration of suspended solids of 70 mg·L$^{-1}$ (1.2 mM), while a pH between 6 and 9 is acceptable. As may be seen from Table 1, that reaction of 0.1 mM $Fe(NO_3)_3$ with a slight excess of fullerenol consistent with an industrial discharge (0.5 mM) resulted in precipitation within 72 h. However, significant cross-linking and suspended particle formation occur at significantly shorter reaction times. It is clear that, under such

conditions, fullerenol effluent would precipitate at some distance from the source. If the resulting aggregates are stable and nontoxic, then exposure of the aquatic environment may result in the "spontaneous remediation" of hydroxyfullerenes. However, on the basis of the foregoing, it is clear that the interaction of hydroxyfullerenes with metals is an important issue with regard to waste treatment, fullerene exposure in the environment, and fullerene-based pharmaceutical agents.

**Supporting Information Available:** SEM, TEM, UV−visible and XPS spectra, and calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The lack of reaction with KCl, HCl, or NaOH suggests that ionic concentration and pH are not associated with the observed reaction.

(11) DLS measurements with dilute solutions (to slow precipitation) suggested that in 30 min, a particle size of 700 nm was formed; however, the concentrations used (0.005 mM) are below the reliability of the instrument.

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