Pentaorgano[60]fullerene $R_5C_{60}^-$. A Water Soluble Hydrocarbon Anion

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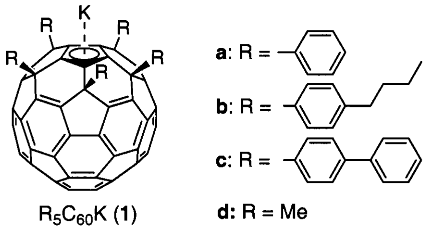
(Received July 3, 2000; CL-000633)

A new class of hydrocarbon anions, pentaaryl- and pentamethylfullerene anions $R_5C_{60}^-$ (R = Ph, 4-BuC_6H_4, 4-PhC_6H_4, Me) was found to be stable and soluble in water. Atomic force microscopic observation and dynamic light scattering measurements indicated that the potassium salt $Ph_5C_{60}K$ in water forms spherical aggregates with an averaged radius of about 17 nm.

In spite of its extreme hydrophobicity, [60]fullerene can be made soluble in water by connecting it to functional groups that are charged in water (e.g., carboxylic acid and amine).[1] Water soluble fullerenes not only exhibit diverse biological activities[1a–f] but also form ordered aggregate structures that can be utilized in materials science.[1g,h] We report here that the pentaaryl- and pentamethylfullerene anions $R_5C_{60}^-$ (R = Ph, 4-BuC_6H_4, 4-PhC_6H_4, Me)[2,3] show remarkable stability and solubility in water.[4] These cyclopentadienides are readily available through the 5-fold addition of organocopper reagent to C_{60}.[2] Being composed solely of carbon atoms and hydrogen atoms, these compounds represent a rare example of hydrocarbon anions with well-defined water solubility. The unique feature of this water-soluble fullerene is that the solubility arises from the charge in the fullerene core rather than that in the pendant side chains as in the previously known water-soluble organofullerenes. Atomic force microscopic (AFM) observation and dynamic light scattering (DLS) measurements of aqueous solutions of the potassium salt $Ph_5C_{60}K$ (**1a**) indicated that **1a** (1.0×10^{-7}–2.0×10^{-3} mol·L^{-1}) in water at 25 °C forms spherical aggregates with an averaged radius of about 17 nm.

In contrast to our previous observation that the D_2O-quenching of the reaction mixture of the 5-fold organocopper ($PhMgBr/CuBr{\cdot}SMe_2$) addition to C_{60} afforded a deuterated compound $Ph_5C_{60}D$,[2a] we found that the potassium pentaarylfullerenide $Ar_5C_{60}K$ (**1a**: Ar = Ph, **1b**: 4-BuC_6H_4, **1c**: 4-PhC_6H_4) prepared from $Ar_5C_{60}H$[2b] and 1 equiv of KO^{t}Bu in THF was stable in water. Namely, dilution of the THF solution with water (pK_a = 15.7) formed a stable homogenous solution.[5,6] The corresponding pentamethyl derivative $Me_5C_{60}K$ (**1d**)[2c] in THF was also stable in water. Taken together, these experiments indicate that the stability of the anions is due to the intrinsically high stability of the cyclopentadienide anion through delocalization of the negative charge toward the 50-π electron system at the bottom of the C_{60} cage through "endohedral homoconjugation"[4] rather than due to steric protection of the cyclopentadienyl anion by the R-substituents against the attack of water or proton (i.e., kinetic stability).

A THF-free aqueous solution of the fullerene cyclopentadienide was prepared as follows: Under argon atmosphere, a portion of the dark red THF solution of $R_5C_{60}K$ (**1**) (3×10^{-3} mol·L^{-1}) was added into degassed ultra pure water [THF : water = 1:10 (v:v)]. The resulting orange solution was concentrated to less than half an original volume, and was diluted with water to the original volume. After the evaporation–dilution cycle was repeated several times, evaporation was continued until precipitation started. Finally, removal of a small amount of the precipitate with centrifuge (1.5×10^4 rpm, 10 min) gave a red-colored clear saturated solution.[7] Approximate concentrations of **1a**, **1b**, **1c**, and **1d** in aqueous solution thus prepared were 5×10^{-3} mol·L^{-1} (6 g·L^{-1}), 1.5×10^{-3} mol·L^{-1} (2.3 g·L^{-1}), 2.6×10^{-3} mol·L^{-1} (3.7 g·L^{-1}), 4.7×10^{-4} mol·L^{-1} (0.37 g·L^{-1}), respectively. Once prepared, these aqueous solutions remained stable for a month under air (as examined by DLS), as opposed to the corresponding THF solutions that were immediately oxidized upon exposure to air into a mixture of several oxidation products. A more dramatic difference between the aqueous solution and the THF solution was observed in the ^{1}H NMR measurements. As reported previously,[2] the ^{1}H NMR spectrum of $Ph_5C_{60}K$ (**1a**) in THF-d_8 showed sharp multiplet signals in the aromatic region indicating C_{5v} symmetry of the molecule. On the other hand, the D_2O solution of the same compound showed no ^{1}H NMR signals at all. In addition, a comparison of the UV/vis spectra of **1a** in THF and H_2O showed significant broadening of the absorption bands in the aqueous solution without significant change in λ_{max} and the absorption intensity (Figure 1). The air-stability and the spectral behavior (^{1}H NMR, UV/vis) are the clear indications of the difference in the macroscopic environment of the anions in the THF and the aqueous solutions, namely, aggregate formation in the latter.



$R_5C_{60}K$ (**1**)

To obtain information on the state of aggregation of the anion, we examined the aqueous solution of $Ph_5C_{60}K$ (**1a**) on mica surface by AFM (Figure 2). Thus, 1 μL of a 5×10^{-4} mol·L^{-1} aqueous solution of **1a** was deposited on mica (5×5 mm^2) under air, and was observed by AFM with an AC mode (JEOL JSPM-4200) with a silicon cantilever (NT-MDT, resonant frequency ~180 kHz). The AFM image showed flat round-shaped objects corresponding to the aggregated **1a**. The size of the aggregates ranges from 40 to 80 nm in diameter and from 5 to 16 nm in height. A typical object in Figure 2 measures 70 nm in diameter and 10 nm in height (see inset). Its volume is roughly estimated at 2.0×10^4 nm^3. This value for the half-spherical object corresponds to a radius of 17 nm for a

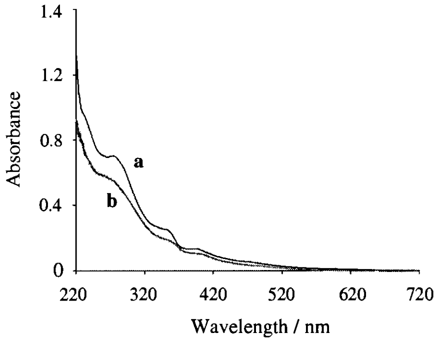


Figure 1. UV-vis absorption spectra of $Ph_5C_{60}K$ (**1a**) in THF (1.0×10^{-5} mol·L^{-1}) (a) and in water (8.0×10^{-6} mol·L^{-1}) (b) .

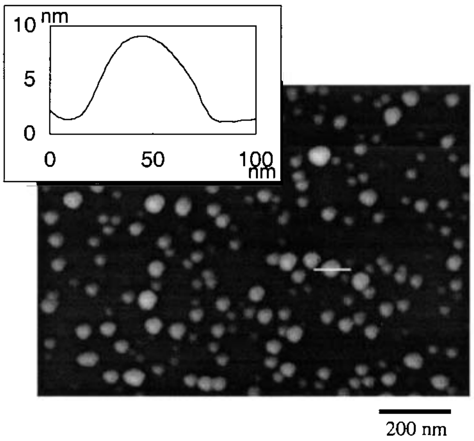


Figure 2. Atomic force microscope image (AC mode) of aqueous $Ph_5C_{60}K$ (**1a**) aggregate on mica. Inset shows height profile corresponding to the line in the image.

spherical object. This estimate of the volume and the size distribution by AFM is in good accord with the results of the light scattering experiment (vide infra). The flat shape of the objects on the mica surface must be due to adsorption force between the aggregates and the mica surface.

To obtain quantitative data on the free-floating aggregates of **1** in aqueous solution, DLS measurements at different scattering angles for the dark orange 2.0×10^{-6} mol·L^{-1} solution of **1a** were carried out to obtain an averaged apparent hydrodynamic radius value of 16.8 nm with a polydispersity index[8] of 0.18 ± 0.02 (Figure 3).[9] The size and size distribution of the particles did not show an apparent angular dependence. In good accordance with the AFM results, the lack of angular dependence shows that the aggregates are globular particles. Samples of much lower concentrations ($\approx 1 \times 10^{-7}$ mol·L^{-1}) prepared by diluting the 2.0×10^{-3} mol·L^{-1} solution gave essentially the same results.

Note that none of the existing models proposed for aggregates of lipid-type amphiphiles could be applied straightforwardly to the aggregation behavior of $R_5C_{60}K$, since, in this unique amphiphile, the large spherical fullerene core represents both the origin of the charge-induced water solubility and that of the hydrophobicity of the molecule. Much remains to be undertaken for elucidation of the aggregate structure at the molecular level.

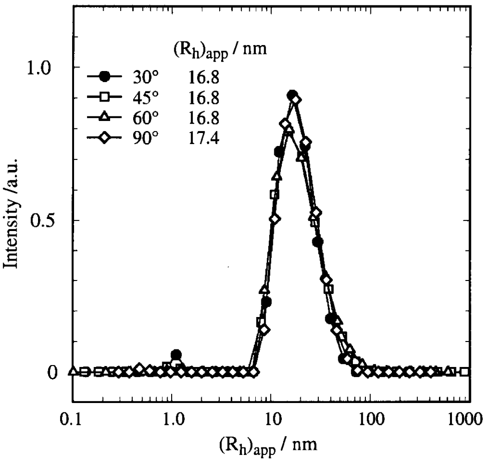


Figure 3. Apparent hydrodynamic radius distribution of $Ph_5C_{60}K$ (**1a**) aqueous solution with $C = 2 \times 10^{-6}$ mol·L^{-1} at different scattering angles.

This research was supported by the Ministry of Education, Science, Sports, and Culture (Monbusho), Grant-in-Aid for Scientific Research on Priority Area (No. 283, Innovative Synthetic Reactions) and by the JSPS/NSF Exchange Program. Generous allotment of computational time from Intelligent Modeling Laboratory and Information Technology Center, the University of Tokyo is gratefully acknowledged. BC gratefully acknowledges partial support of this work by the US National Science Foundation (DMR 9984102).

References and Notes

1 a) H. Tokuyama, S. Yamago, E. Nakamura, T. Shiraki, and Y. Sugiura, *J. Am. Chem. Soc.*, **115**, 7918 (1993). b) S. Yamago, H. Tokuyama, E. Nakamura, K. Kikuchi, S. Kananishi, K. Sueki, H. Nakahara, S. Enomoto, and F. Ambe, *Chem. Biol.*, **2**, 385 (1995). c) E. Nakamura, H. Tokuyama, S. Yamago, T. Shiraki, and Y. Sugiura, *Bull. Chem. Soc. Jpn.*, **69**, 2143 (1996). d) A. S. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, and C. Hélène, *Angew. Chem., Int. Ed. Engl.*, **33**, 2462 (1994). e) Y.-Z. An, C.-H. B. Chen, J. L. Anderson, D. S. Sigman, C. S. Foote, and Y. Rubin, *Tetrahedron*, **52**, 5179 (1996). f) S. Takenaka, K. Yamashita, M. Takagi, T. Hatta, A. Tanaka, and O. Tsuge,, *Chem, Lett.*, **1999**, 319. g) A. M. Cassell, W. A. Scrivens, and J. M. Tour, *Angew. Chem., Int. Ed. Engl.*, **37**, 1528 (1998). h) H. Murakami, M. Shirakusa, T. Sagara, and N. Nakashima, *Chem. Lett.*, **1999**, 815.

2 a) M. Sawamura, H. Iikura, and E. Nakamura, *J. Am. Chem. Soc.*, **118**, 12850 (1996). b) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organometal. Chem.*, **599**, 32 (2000). c) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, and E. Nakamura, *Chem. Lett.*, **2000**, 262. d) M. Sawamura, H. Iikura, A. Hirai, and E. Nakamura, *J. Am. Chem. Soc.*, **120**, 8285 (1998).

3 For sol formation by air oxidation of C_{60}^- and C_{70}^- in aqueous phase, see: a) X. Wei, M. Wu, L. Qi, and Z. Xu, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1389. b) X. Wei, Z. Suo, K. Zhou, Z. Xu, W. Zhang, P. Wang, H. Shen, and X. Li, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 121.

4 H. Iikura, S. Mori, M. Sawamura, and E. Nakamura, *J. Org. Chem.*, **62**, 7912 (1997).

5 The addition of aq NH_4Cl caused phase separation. The separated material was extracted with toluene and was found to be $Ph_5C_{60}H$ (>99% purity) by HPLC analysis.

6 Owing to the extreme insolubility of $Ph_5C_{60}H$, we were unable to measure equilibrium acidity in aqueous solution. From this reason of insolubility, the protonation of **1a** with NH_4Cl/H_2O (footnote 5) only indicates that NH_4Cl is acidic enough to at least partially protonate **1a**, while H_2O is completely unable to protonate it, and this fact does not mean at all that the pK_a value of $R_5C_{60}H$ is higher than the pK_a value of NH_4^+ (9.2).

7 The ^1H NMR spectrum indicated that the amount of remaining THF is negligible. Once solidified by entire removal of solvent, $Ph_5C_{60}K$ could not be redissolved in water.

8 B. Chu, “Laser Light Scattering,” Academic Press, CA (1991), Chap. 7.

9 The results were reproducible after keeping the samples over one month.