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Advanced materials: fluorous fullerenes and nanotubes

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Abstract—This paper describes the preparation and properties of several fluorous-substituted fullerene and fullerene nanotube materials. Several of these are quite fluorous soluble and, due to the insulating effect of $-CH_2-$ groups between the perfluorocarbon pony tails and the fullerene ring system, they exhibit electronic and photophysical properties similar to non-fluorous fullerenes. Certain unique applications of these hybrid materials are discussed. © 2002 Published by Elsevier Science Ltd.

1. Introduction

There has been great interest recently in the design and synthesis of hybrid materials, particularly materials combining the desirable properties of two distinct classes of compounds. Since the first discovery of fullerenes,[1] the idea of perfluorinating C_{60} (Fig. 1(A)) was discussed. The structure of the completely fluorinated compound, $C_{60}F_{60}$ (Fig. 1(B)), can be compared to Telfon (Fig. 1(C)) and not surprisingly the prospect for producing nanoscale ball bearings ('Teflon Buckyballs') attracted the attention of many chemists. Such materials were expected to combine unique physico-chemical properties of both fullerenes and fluorocarbons, resulting in a new material with novel properties such as overall inertness, and desirable surface and electrochemical characteristics.

Direct fluorination of the fullerene-C_{60} cage was chosen as the route for synthesis of perfluorinated fullerene $C_{60}F_{60}$—a compound that was expected to be a superlative lubricant because of its Teflon-like surface properties and spheroidal shape. Prior to synthetic work, theoretical calculations were reported that predicted the possible existence of the $C_{60}F_{60}$ molecule. Calculations done by Scuseria[2] predicted stability of such a molecule, however a second report by Cioslowski,[3] using similar calculations, concluded that the $C_{60}F_{60}$ might not be readily isolable. Subsequently, several experimental papers have been published attempting to prepare this material. Holloway et al.[4] reported a stepwise fluorination leading to, among other partially fluorinated products, an 'almost white' material that was speculated to be $C_{60}F_{60}$ based on NMR analysis (a single sharp ^{19}F-line). No mass-spectral data supported this speculation and this result has never been independently confirmed.[5,6]

What has been shown repeatedly elsewhere is that, depending

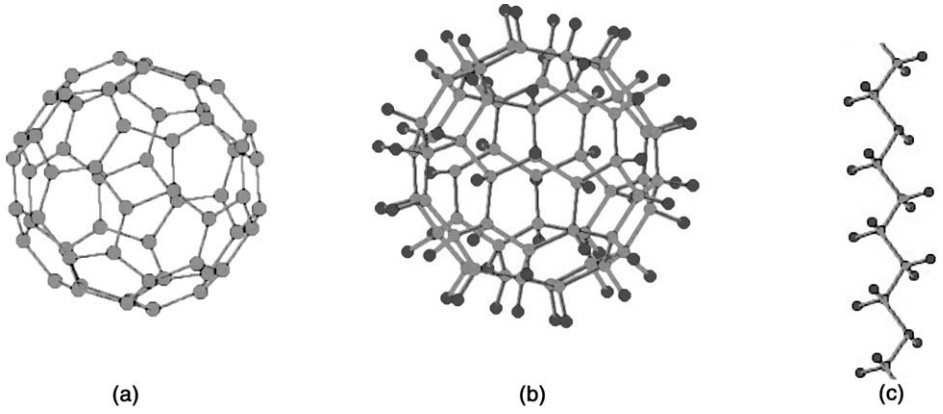

Figure 1. (a) Fullerene-C_{60}, (b) $C_{60}F_{60}$, (c) Teflon (polytetrafluoroethylene).

Keywords: fullerenes; isomer; Diels–Alder reaction.

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Figure 2. X-Ray crystal structure of $C_{60}F_{18}$ (from Ref. 11).

on fluorination conditions, the products usually are a mixture of partially fluorinated fullerenes of general formula $C_{60}F_{2n}$. In addition and perhaps surprisingly, a series of hyperfluorinated products $C_{60}F_{2n}$ with $n>30$ are also observed, which are believed to be open-cage fullerene structures.[7] The mixtures of fluorination products were difficult to separate and only three major stable products with formulas $C_{60}F_{48}$,[8] $C_{60}F_{36}$[9] and $C_{60}F_{18}$[10] have been isolated and fully characterized.

Most recently, an improved procedure for the preparation of the latter compound $C_{60}F_{18}$ and its X-ray crystal structure was reported.[11] The compound is a 'deflated ball' structure with one half of the fullerene cage flattened (Fig. 2).

All fluorine atoms are attached on the same side of the buckyball and this particular substitution pattern yields a true benzenoid ring on a flattened fullerene surface. It is this stability factor that is believed to be responsible for stability of the most commonly observed fluorofullerene structures. $C_{60}F_{36}$ and $C_{60}F_{48}$ have three and four π-delocalized benzenoid rings, respectively. $C_{60}F_{60}$ (Fig. 1(B)) has never been produced, moreover evidence now suggests that it is unstable towards 'cracking' of the fullerene-C_{60} cage.

Fluorinated fullerenes (with fluorines directly attached to the cage) are also quite reactive towards nucleophiles,[12] for example, some react exothermally with water, displacing the fluorines for hydroxyl groups. In addition, many fluorination reactions proceed with poor yields and

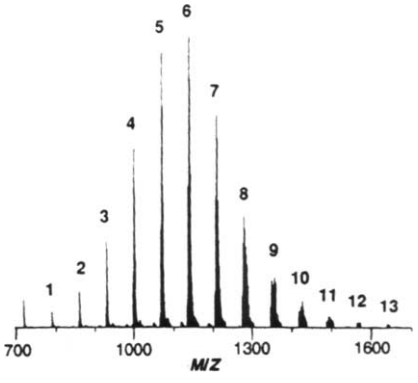


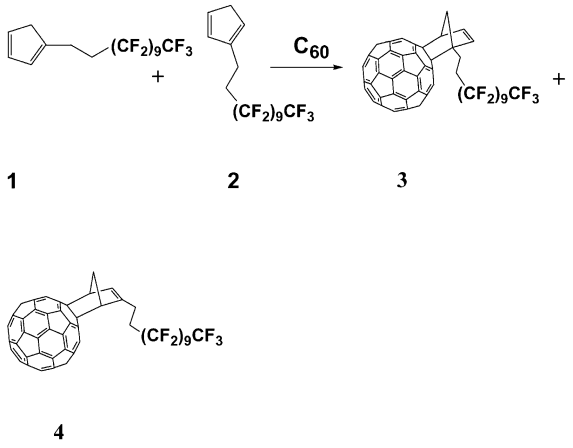
Figure 3. Mass spectrum of a mixture of C_{60}-Rf_n showing the complex mixture of products. Peaks 1–13 are $C_{60}[(CF_2)_5CF_3]_n$ where n=1–13, respectively, (adapted from Ref. 13).

selectivity, resulting mostly in highly perfluoro-derivatized fullerenes with the additional complication of oxygen incorporation (as epoxides or hydroxyls). Thus, the observed properties of these materials make fluorinated fullerenes unsuitable for their hypothesized role as superlubricants, however they could be potentially interesting intermediates for fullerene functionalization.

The search for hybrid fullerene/Teflon lubricant materials did not stop there however. The Dupont group, led by Fagan, reported[13] the preparation of perfluoroalkylated fullerenes by means of thermal or photochemical decomposition of perfluoroalkyl iodides and perfluoroalkyldiacyl peroxides. Up to 16 perfluoroalkyl chains have been reported to be added to C_{60} (Fig. 3.) The composition of the mixture of products was shown to be dependent on the conditions and perfluoroalkyl reagents used in reaction. None of the specific compounds has been isolated since these products are a complex mixture of isomeric compounds. The reported products were found to be quite thermally stable (up to 270°C), soluble in fluorous solvents, and chemically resistant to corrosive aqueous solutions. The resulting products were found to be volatile enough to be prepared in a thin film that exhibited surface properties of perfluoroalkylated materials (Teflon).[14]

2. Results and discussion

We began a study of fluorous solubilization of fullerene compounds, by the application of well-known fullerene chemistry.[15] Taking our clue from the Teflon pony tail work of Curran,[16] our first experiments[17] focused on applying fullerene-C_{60} as a dienophile[18] in the Diels–Alder reaction. We decided to examine a fluorous reagent 1,3-cyclopentadiene **1** and **2** with a perfluoroalkyl side chain and an ethylene spacer to insulate the diene from the electron-withdrawing effect of its perfluorinated part. Similar dienes have already been reported and we followed the method of Hughes and Trujillo.[19] Compounds **1** and **2** were prepared from freshly prepared cyclopentadienyl sodium and 1*H*,1*H*,2*H*,2*H*-perfluorododecyl iodide and the product was found to be a mixture of two isomers **1** and **2** (1:1 ratio). Since conditions could not be found to separate them, the mixture was used in the subsequent Diels–Alder experiments.[17] When 2 equiv. of fluoroalkylated dienes were reacted with 1 equiv. of C_{60} at room temperature overnight, the Teflon pony tailed monoaddition products **3** and **4** could be isolated. As expected, the isomers could be readily distinguished by ^{1}H NMR, revealing a **3** to **4** ratio of approximately 1.5 to 1 indicating a slight reactivity preference for compound **3**, perhaps due to an electron withdrawing effect on this diene isomer. Unfortunately, one perfluoroalkyl chain was not enough to render the fullerene adducts **3** and **4** soluble in perfluorocarbon solvents. Attempts to prepare multiple fullerene Diels–Alder adducts resulted in an unseparable mixture of isomers, consisting of not only isomeric adducts from the starting diene reagent, but the formation of regioisomeric bis, tris, and higher fullerene adducts.[20] While the mixtures were soluble in perfluorocarbon solvents, no conditions could be found to separate individual constituents. Elemental analysis (carbon/fluorine) indicated that the average

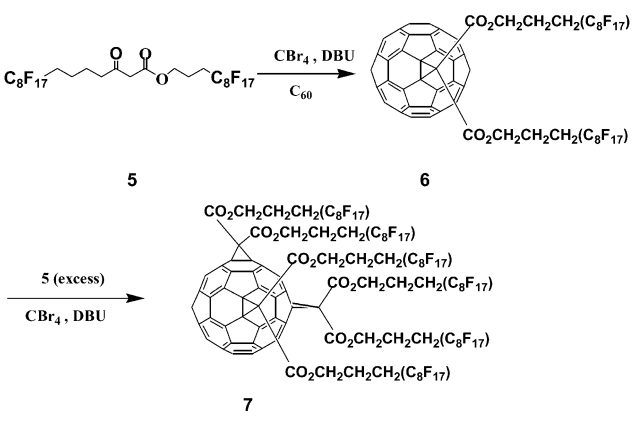


Scheme 1.

formula of the product to be about C_{60}[diene]$_{2.3}$. In addition, the analysis indicated a large amount of oxygen present. MALDI-TOF mass spectrometry of the crude mixture revealed extensive oxidation of the fullerene core, in some cases up to 15 oxygen atoms could be clearly seen.[17] Thus a practical preparation of C_{60}–Teflon hybrids by means of Diels–Alder reaction proved unsuitable (Scheme 1).

In a second approach, we decided to use a different reaction for fullerene functionalization, as well as devise a 'fluorous' reagent that would introduce more than one perfluoroalkyl group at a time. Our synthetic strategy employed the important fullerene functionalization reaction known as the Hirsch–Bingel reaction.[20,21] This process as been well-studied and broadly utilized for fullerene derivatization.[15] For introduction of fluoroalkyl chains onto C_{60}, we incorporated a three carbon spacer to insulate the electron withdrawing effect of the fluoroalkyl chain (Scheme 2).[22]

We reacted 3-perfluorooctyl propyl alcohol with malonyl dichloride to yield a fluorous-soluble malonate **5** in 68% yield. The Hirsch–Bingel reaction was carried out on the mixture of malonate **5**, CBr_4, DBU, and C_{60} in toluene to yield monoadduct **6** in 35% yield. Compound **6** was fully characterized as a C_{60} monoadduct by ^{1}H NMR, ^{19}F NMR, MALDI ($C_{85}F_{34}O_4H_{12}$: m/z=1741), IR, UV–Vis, and elemental analysis. The compound showed good solubility in Freon 113, but virtually no solubility in fully fluorinated



Scheme 2.

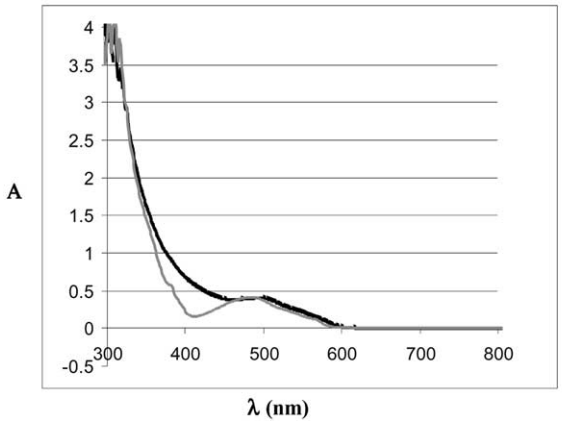
Figure 4. (a) Water droplet on untreated Teflon film. (b) Water droplet on Teflon film, treated with compound **6** (Note changes in contact angle of droplet between a and b).

solvents such as FC-72 (a mixture of perfluorohexanes) and FC-75 (a mixture of perfluorooctanes).

Despite the lack of fluorous solubility, this compound behaves as a hybrid 'amphiphilic' fullerene–Teflon compound. The compound forms organic/fluorous emulsions, and as one might expect could form self-assembled mono-layers on Teflon materials. Indeed, compound **6** can coat a (solid) Teflon surface (Fig. 4(A) and (B)) showing changes in contact angles for drops on the surface that suggest the expected surface modification.

Using the same reaction, we could introduce even more fluorous chains. Multiple malonate additions to C_{60} is known to occur with formation of two major tris-adduct isomers with C_3 and D_3 symmetry,[20,21] and in the C_3 isomer all malonate addends on the fullerene ball are positioned equatorial. Thus the reaction of C_{60} with 3.3 equiv. of malonate **5**, CBr_4, and DBU was carried out, this time in a mixture of benzene/Freon, giving the desired tris-adduct **7** in 14% yield.

The MALDI mass-spectra showed a molecular ion for $C_{135}F_{102}O_{12}H_{36}$: at m/z=3784 as well as a UV–Vis spectra (Fig. 5) for the orange-red C3 fluorous tris-adduct **7** which was virtually identical to that of the known[20] ethyl ester fullerene tris-adduct **8** (Fig. 5) Fluorous compound **7** is very soluble in perfluorinated solvents and to a much lesser extent in more common organic solvents [the fluorous/organic partition coefficient is ρ=0.94 (FC-75/toluene)].[22] This C_3 symmetric methanofullerene compound **7** contains six 'Teflon pony tails' directed towards one side of the fullerene ball, and thus might be expected to self-organize at a fluorous interface even better than compound **6**. In addition, insulation of the electron density of fluorous pony tails and C_{60} allows the properties of fullerene ball, such as generation of singlet oxygen to remain largely intact. Having in hand a pair of both fluorous soluble and insoluble C3 tris fullerene derivatives, we were able to compare the ability of these materials to sensitize singlet molecular oxygen generation in both fluorous and organic solvents. We have recently reported that compounds **7** and **8** sensitize the formation of singlet molecular oxygen with almost the same quantum yields [quantum yield (Φ_Δ)=0.40 (toluene for **8**) and 0.45 (n-C_6F_{14}) for **7**].[22] In addition, the measured lifetime for singlet molecular oxygen in perfluorohexane is very long (7000 μs), compared to 24 μs in benzene. In light of current interest in fullerenes for photodynamic therapy (PDT)[23] and the use of fluorous-phase artificial blood substitutes,[24]



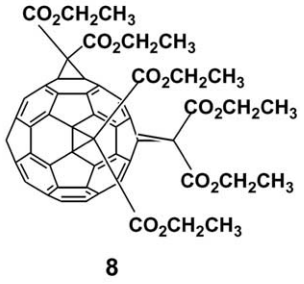
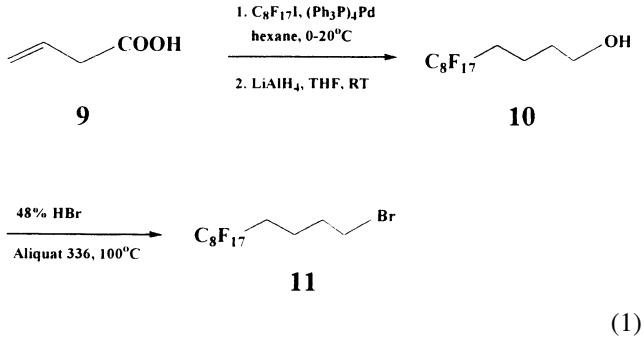


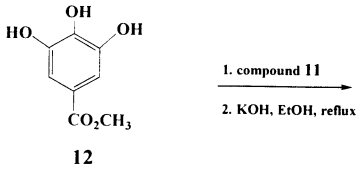
Figure 5. UV–Vis for ethyl ester tris-adduct **8** in benzene (gray line) and for flourous tris-adduct **7** in C_6F_{14} (black line).

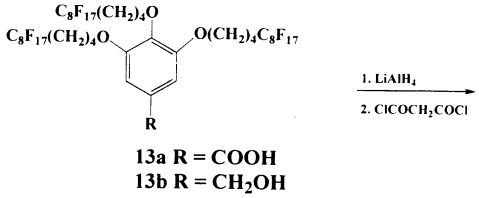
these facts suggest a potential role for fluorous fullerene photosensitizers.

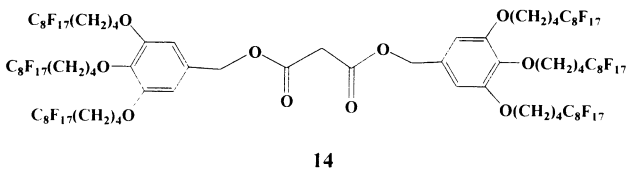
Finally, we have extended our fluorous fullerene experiments in two additional directions. First of all, we have considered the preparation of a fluorous fullerene dendrimer mono-adduct. Given the fact that six fluorous chains appear to be necessary to balance organic/fluorous partitioning of the fullerene ball, we have prepared monoadducted fluorous dendrofullerene **15** via malonate compound **14**.



(1)



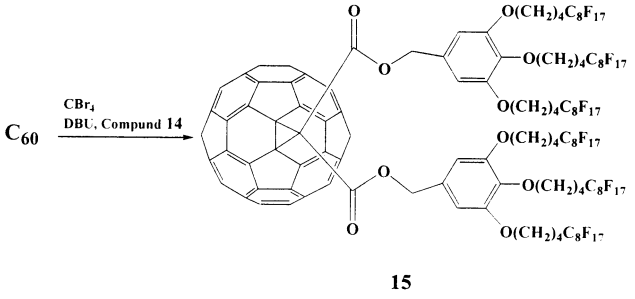




(2)

Palladium catalyzed addition of perfluorooctyl iodide to 3-butenoic acid **9** followed by lithium aluminum hydride reduction gives alcohol **10**,[25] which can be converted into bromide **11** with HBr (Eq. (1)). Alkylation of ester **12**, followed by hydrolysis gave acid **13a**, which was reduced with lithium aluminum hydride to alcohol **13b** and then reacted with malonyl dichloride to give malonate compound **14** (Eq. (2)).

Compound **14** was used in a Hirsch–Bingel reaction with fullerene-C_{60} to produce a very fluorous soluble mono-adduct **15**, a compound currently under investigation.



(3)

This substance is likely to provide insights on the relationship of substitution vs. properties, since fullerene mono-adducts (such as **15**) generally exhibit chemical and physical properties closer to C_{60} itself than tris-adducts (such as **7**).

We have also been engaged in a program to solubilize fullerene nanotubes (single-walled nanotubes, SWNT) in various solvents,[26] and have some interesting preliminary results. Using the Zonyl perfluorocarbon co-polymer **16** reported by Bergbreiter,[27] we have prepared a hybrid perfluorocarbon-nanotube material that is Freon soluble. SWNTs were cut (oxidized) using established methods,[28] leading to SWNTs terminated with –COOH groups. Several derivatization experiments with this material has been reported, in particular, amide formation.[29] Our own work

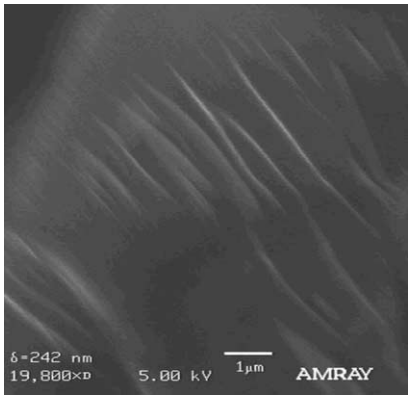
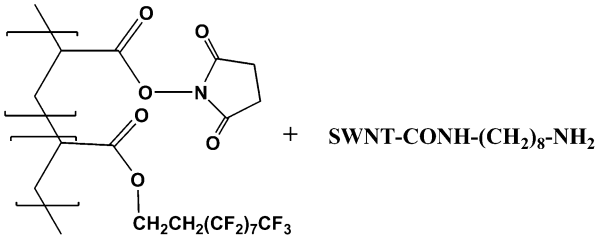


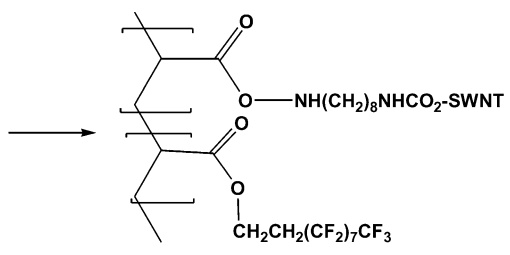
Figure 6. SEM picture of Zonyl-co-polymer SWNT hybrid material **18** (poured film) using AMRAY 1850 field emission scanning electron microscope.

has reported the formation of SWNT-COCl by reaction of SWNT-COOH with thionyl chloride, and its reaction with 1,8-diamino-octane to give SWNT amine **17**. The resulting amine-functionalized nanotubes were reacted with various dyes.[30]

For preparation of fluorous hybrid nanotubes, we reacted amine-functionalized nanotube material **17** with a Zonyl perfluorocarbon co-polymer **16** (prepared as reported[27] from 1:20 *N*-acryloyloxysuccinimide/zonyl fluoromonomer) via its pendant hydroxy-succinate groups to produce **18**. The resulting material is a gray amorphous solid, freely soluble in Freon, but not obviously soluble in FC-75. On the other hand, Freon-soluble material was examined in the scanning electron microscope to reveal nanotube-like features (Fig. 6, Scheme 3).



16 **17**



18

Scheme 3.

3. Experimental

3.1. Data for compounds

3.1.1. Synthesis of fluorous alcohol 10. A solution of vinylacetic acid (2.7 g, 31.7 mmol) in 50 ml of hexane was cooled to 0°C under N_2 and *N*-perfluorooctyl iodide (15.8 g, 28.9 mmol) and $(Ph_3P)_4Pd(0)$ (1.5 g, 1.2 mmol) were added. The reaction was stirred for 6 h whereupon a yellowish-orange solution resulted. At this time, the reaction mixture was washed with water and the hexane layer dried over anhydrous magnesium sulfate. Evaporation of the solvent resulted in 17.8 g yellowish crystals. This intermediate product was dissolved in 100 ml of freshly distilled THF and added to slurry of $LiAlH_4$ (4.2 g, 112.7 mmol) in 50 ml of freshly distilled THF. The reaction mixture was left stirring for 4 h at room temperature and then was quenched by addition of water. The resulting precipitate was filtered and washed with cold water. The product was purified by sublimation at 40°C resulting in 6.4 g of pure product **10** (white crystals, 45.7% yield). ^{1}H NMR ($CDCl_3$, δ): 3.71 (t, 2H); 2.17 (m, 2H); 1.69 (m, 4H). ^{13}C NMR ($CDCl_3$, δ): 120–115 (indistinguishable cluster of peaks due to $-CF_2-$ groups), 62.75, 32.49, 31.33, 17.45. FT-IR (cm^{-1}): 3420m, 2957w, 2860w, 1458w, 1374w, 1334w, 1246vs, 1209vs, 1148s, 1135w, 1117w, 1058m, 1021m, 972m, 705m, 660m. MS calcd for $C_{12}H_9F_{17}O$: 492; Found (MH+): 493.

3.1.2. Synthesis of fluorous bromide 11. Alcohol **10** (5.0 g, 13.2 mmol) was mixed with 6.2 ml (47 mmol) of 48% HBr solution and 0.2 g (0.4 mmol) of Aliquat® 336. The reaction was refluxed at 100°C for 20 h, then cooled, and the product extracted from the reaction mixture with Freon 113. White crystals (4.1 g) were isolated in 73.1% yield. ^{1}H NMR ($CDCl_3$, δ): 3.43 (t, 2H); 2.11 (m, 2H); 1.95 (m, 2H); 1.82 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): 120–115 (indistinguishable cluster of peaks due to $-CF_2-$ groups), 32.85, 32.46, 30.68, 19.64. FT-IR (cm^{-1}): 2962w, 2863w, 1467w, 1436w, 1394w, 1244vs, 1206vs, 1149s, 1135m, 1116m, 1066w, 1016w, 705m, 661m. MS calcd for $C_{12}H_9F_{17}Br$: 554; Found (MH+) 555.

3.1.3. Synthesis of fluorous acid 13a. A solution of 0.37 g (2.0 mmol) methyl 3,4,5-trihydroxybenzoate, 2.44 g potassium carbonate, and 4.40 g (8 mmol) of bromide **11** in 47 ml of DMF was heated to 65°C under nitrogen and stirred overnight. Upon completion of the reaction (TLC), the mixture was poured into 300 ml of water, providing yellowish crystals which were extracted several times with FC-72 (mixture of perfluorohexanes). The material was then recrystallized from acetone, and then hydrolyzed by addition to 25 ml of 95% ethanol and 2.5 ml of 10N aqueous KOH solution. After refluxing for 6 h, the mixture was cooled to room temperature and neutralized with aqueous HCl. The reaction mixture was extracted several times with Freon 113. After evaporation of the Freon, the yellowish residue was redissolved and chromatographed on silica-gel using ethyl acetate/hexane (25:75): Product fractions afforded 2.3 g of yellowish crystals of **14** in 71% yield. ^{1}H NMR ($CDCl_3$, δ): 7.32 (s, 2H); 4.02 (m, 6H); 2.11 (m, 6H); 1.95 (m, 12H). ^{13}C NMR ($CDCl_3$, δ): 153.05, 130.42, 129.74, 124.45, 123.76, 119.49, 118.75, 118.48, 117.98, 113.44, 112.68, 111.94, 109.21, 68.92, 30.76, 29.29, 17.87. FT-IR (cm^{-1}): 2935w,

2868w, 1713s, 1446w, 1421w, 1374w, 1335w, 1250m, 1238m, 1207vs, 1147s, 1135w, 1113m, 1085, 1055, 986, 965, 935, 839, 661m, 648m, 622, 602, 578, 529m. MS calcd for $C_{43}H_{27}F_{51}O_5$: 1592: Found (MH+) 1593.

3.1.4. Synthesis of fluorous alcohol 13b. An anhydrous THF solution of 2.3 g (1.4 mmol) of acid **13a** was added dropwise to a slurry of $LiAlH_4$ (0.22 g, 5.70 mmol) in 20 ml of anhydrous THF. The reaction was stirred for 4 h at room temperature. Upon completion of the reaction, the mixture was carefully quenched with water, and acidified with aqueous HCl. The product alcohol **13b** was extracted with Freon 113 and isolated after a separation on silica-gel ethyl acetate/hexane. In some cases products of over-reduction was observed (R=CH_3). This procedure afforded 1.1 g of pure alcohol **13b** as white crystals (42% yield). ^{1}H NMR ($CDCl_3$, δ): 6.52 (s, 2H); 4.54 (s, 2H); 3.96 (m, 6H); 2.12 (m, 6H); 1.89 (m, 12H). ^{13}C NMR ($CDCl_3$, δ): 130.43, 129.72, 124.45, 123.76, 119.52, 118.75, 118.48, 117.79, 113.44, 112.69, 111.94, 105.93, 68.84, 30.95, 29.42, 17.65. FT-IR (cm^{-1}): 3323w, 2952w, 2889w, 1592w, 1370w, 1334w, 1245s, 1205vs, 1152s, 703w, 656m. MS calcd for $C_{43}H_{29}F_{51}O_4$: 1578: Found (MH+) 1579.

3.1.5. Synthesis of fluorous malonate 14. A solution of 0.7 g (0.4 mmol) of alcohol **13b** was prepared in a mixture of 20 ml of freshly distilled anhydrous CH_2Cl_2 and 5 ml of Freon 113. To that mixture, excess anhydrous pyridine was added (0.4 ml, 4.3 mmol) under Ar, followed by 20 μl (0.2 mmol) freshly distilled malonyl dichloride. After 2 h reaction the color changed from yellow to green to purple, at which time the reaction mixture was carefully quenched with water, and then extracted several times with FC-72. Evaporation of the solvent resulted in a purple solid. (The purple color is often observed in malonyl dichloride reactions and is presumably due to polyaromatic impurities) The light color can be easily removed by treatment with activated charcoal, yielding in 0.44 g of white crystals of **14** (65% yield). ^{1}H NMR ($CDCl_3$, δ): 6.46 (s, 4H); 5.01 (s, 4H); 3.95 (t, 4H); 3.89 (t, 8H); 3.40 (s, 2H); 2.06 (m, 12H); 1.86 (m, 24H). All attempts to obtain ^{13}C NMR spectra failed due to a low solubility of malonate **14** in common organic deuterated solvents. FT-IR (cm^{-1}): 2967m, 2929s, 2858m, 1756w, 1735m, 1596w, 1507w, 1467m, 1443m, 1377w, 1337w, 1260vs, 1243m, 1205s, 1150s, 1135m, 1117m, 1052w, 1023m, 875w, 820m, 803m, 747w, 705w, 661m. MS Calc for $C_{89}H_{58}F_{102}O_{10}$: 3225: Found (MH+) 3226.

3.1.6. Synthesis of a fluorous fullerene mono-adduct 15. A solution of 28 mg (0.04 mmol) of C_{60} was prepared in 20 ml toluene and 5 ml Freon 113. To that mixture, 20 mg (0.06 mmol) of CBr_4 was added, followed by 200 mg (0.06 mmol) of malonate **14** and excess DBU. Reaction was stirred at room temperature for 1 h and monitored by TLC. Upon completion, the reaction was quenched with water and washed with Freon 113. The washes were collected and the solvent was removed resulting in a brown solid material, which consisted of mixed products (as was revealed by TLC). Pure mono-adduct **15** was isolated from a silica-gel column, eluting with a 80:1:1 mixture of α,α,α-trifluorotoluene, FC-72, and ethyl acetate to provide 73 mg of **15** as a brown solid, 45.2% yield). ^{1}H NMR ($CDCl_3$, δ): 6.52 (s, 4H); 5.39 (s, 4H); 3.94 (m, 12H); 2.12 (m, 12H); 1.76 (m, 24H). All attempts to obtain ^{13}C NMR spectrum failed due to a low solubility of compound **15** in common deuterated organic solvents. FT-IR (cm^{-1}): 2957, 2928, 2867m, 1751m, 1246s, 1206vs, 1148s, 1148s, 1135w, 1117w, 1069w, 1032w, 705w, 656m. The UV–Vis spectrum in Freon 113 shows a peak at 424 nm characteristic of fullerene monoadducts. MS calcd for $C_{145}H_{56}F_{102}O_{10}$: 3845: Found (MH+) 3946.

3.2. Preparation of nanotube derivative 18

Following the procedure of Bergbreiter,[28] the Dupont fluoroacrylate monomer Zonyl (20 equiv.) was copolymerized in 1-butanol with *N*-acryloyloxysuccinimide (1 eg) using 1–2% 2,2′-azoisobutyronitrile as initiator. After approximately 48 h reflux at 70°C, fluoropolymer **16** precipitated. After cooling, the waxy solid was decanted and air dried (55–60% yield). The material was characterized by IR, which indicated a peak at 1650 cm^{-1} (m) for the amide group and a broad, intense peak at 1725 cm^{-1} for the ester group. Peaks at 1150 and 1250 cm^{-1} were indicative of the Zonyl fluoroacrylate backbone. Next, a fluorous biphasic system containing excess hydrazide-derivatized nanotubes **17** (prepared as described in Ref. 30) suspended in THF and the Zonyl copolymer **16** in Freon was stirred and shaken vigorously, leading to a clear gray solution. After a prolonged period of stirring (several days), the nanotube-fluoropolymer **18** precipitated from solution. The nanotube-fluoropolymer **18** was dispersed in Freon to give a cloudy-gray to black solution with some precipitate. After centrifuging the solution for approximately 15 min, a black precipitate and clear, dark gray supernatant was collected. The gray solution was evaporated to give **18** as a gummy residue. The UV–Vis (Freon) showed a strong peak at 235 nm and small peaks in the region of 265 and 280 nm in a solution of 1,1,2-trichlorotrifluoroethane. A Freon solution of this material was evaporated and examined by SEM (Fig. 6).

4. Conclusions

In summary, several lessons have been learned in the preparation of hybrid fullerene-perfluorocarbon systems. First, while two fluorous chains are not sufficient to impart fluorous solublity to the buckyball, six fluorous chains appear to be adequate. Second, at least three insulating –CH_2– groups fully protect the fullerene sphere from the electron-withdrawing effect of the fluorine atoms as evidenced by identical electronic and photophysical properties. We have shown in this paper that well-characterized hybrid Teflon-fullerene compounds can be prepared and fully characterized. We have also shown these materials present potentially useful novel properties (photosensitization and surface effects). We are continuing work in this area.

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References

1. Kroto, H. W.; Heath, J.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
2. Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 423.
3. Cioslowsky, J. *Chem. Phys. Lett.* **1991**, *181*, 68.
4. Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, J. T.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 9666.
5. Selig, H.; Lifshitz, C.; Perez, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P.; Smith, A. B. *J. Am. Chem. Soc.* **1991**, *113*, 5475.
6. Tuinman, A. A.; Mukherjee, P.; Adcock, J. L. *J. Phys. Chem.* **1992**, *96*, 7584.
7. Tuinman, A. A.; Gakh, A. A.; Adcock, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 5885.
8. (a) Gakh, A. A.; Tuinman, A. A.; Adcock, J. L.; Sachleben, R. A.; Compton, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 819. (b) Boltalina, O. V.; Sidorov, L. N.; Bagryantsev, V. A.; Seredenko, V. A.; Zapolskii, A. S.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2275.
9. Boltalina, O. V.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 649.
10. Boltalina, O. V.; Markov, V. Yu.; Taylor, R.; Waugh, W. P. *Chem. Commun.* **1996**, 2549.
11. Neretin, I. S.; Lyssenko, K. A.; Yu, M.; Slovokhotov, Y. L.; Boltalina, O. V.; Troshin, P. A.; Lukonin, A. Y.; Sidorov, L. N.; Taylor, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3273.
12. Taylor, R.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M.; Holloway, J. H.; Hope, E. G.; Langley, G. J. *Nature* **1992**, *355*, 27.
13. Fagan, P. J.; Krusic, P. J.; McEwen, C. N.; Lazar, J.; Parker, D. H.; Herron, N.; Wasserman, E. *Science* **1993**, 262.
14. Fagan, P. J.; Krusic, P. J.; Wasserman, E. Fluoroalkylated Fullerene Compounds. US Patent 5,354,926, 1994.
15. Wilson, S. R.; Schuster, D. I.; Nuber, B.; Meier, M. S.; Maggini, M.; Prato, M.; Taylor, R. Organic Chemistry of Fullerenes. In *Fullerenes: Chemistry, Physics, and Technology*, Kadish, K., Ruoff, R., Eds.; Wiley: New York, 2000.
16. Struder, A.; Hadad, S.; Ferrito, R.; Kim, S.-Y.; Jeger, O.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823.
17. Wilson, S. R.; Yurchenko, M. E.; Schuster, D. I.; Khong, A.; Saunders, M. *J. Org. Chem.* **2000**, *65*, 2619.
18. Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296.
19. Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15* (1), 286.
20. Hirsch, A.; Lamparth, I.; Karfunkul, H. R. *Angew. Chem., Int. Ed.* **1994**, *33*, 437.
21. Hirsch, A.; Lamparth, I.; Grösser, T.; Karfunkel, H. R. *J. Am. Chem. Soc.* **1994**, *116*, 9385.
22. Wilson, S. R.; Yurchenko, M. E.; Schuster, D. I.; Yurchenko, E.; Sokolova, O.; Braslavsky, S. E.; Klih, G. *J. Am. Chem. Soc.* **2002**, *124*, 1977–1981.
23. *Photodynamic Therapy; 2nd and 3rd Generation Photosensitizers*, Moser, J. G., Ed.; G and B Science: Reading, MA, 1998.
24. (a) Nucci, M. L.; Abuchowski, A. *Sci. Am.* **1998**, 61–65. (b) Whitney, J. D. *Heart Lung* **1989**, *18*, 466–471. (c) Paris, C. L. *Retina* **1991**, *11*, 301. (d) Shaffer, T. H. *Artif. Cells Blood Substit. Immobil. Biotechnol.* **1994**, *22*, 315. (e) Cox, C. A. *Neonatal Netw.* **1996**, *15*, 31. (f) Lowe, K. C. *Artif. Cells Blood Substit. Immobil. Biotechnol.* **2000**, *28* (1), 25–38.
25. Wilson, S. R.; Tan, X. unpublished results.
26. Sun, Y.; Wilson, S. R.; Schuster, D. I. *J. Am. Chem. Soc.* **2001**, *123*, 5348.
27. Bergbreiter, D. E.; Franchina, J. G. *Chem. Commun.* **1997**, 1531.
28. Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.
29. Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.
30. Sun, Y.; Wilson, S. R.; MacMahon, S.; Schuster, D. I. *Proc. Electrochem. Soc.* **2000**, 282.