Organic Functionalization and Optical Properties of Carbon Onions

5 AUTHORS, INCLUDING:

Vasilios Georgakilas
University of Patras
78 PUBLICATIONS **5,859** CITATIONS

SEE PROFILE

Raffaella Signorini
University of Padova
81 PUBLICATIONS **1,345** CITATIONS

SEE PROFILE

Renato Bozio
University of Padova
169 PUBLICATIONS **3,148** CITATIONS

SEE PROFILE

Organic Functionalization and Optical Properties of Carbon Onions

Vasilios Georgakilas,[†] Dirk M. Guldi,*,[‡] Raffaella Signorini,[§] Renato Bozio,*,[§] and Maurizio Prato*,[†]

Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa, 1, 34127 Trieste, Italy, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, I-35131 Padova, Italy

Received January 22, 2003; E-mail: prato@units.it

The arc discharge experiments, developed in recent years to produce large quantities of carbon allotropes, yield fullerenes and nanotubes as the most abundant species. In addition, other forms of carbon are obtained, usually labeled as "amorphous carbon" or "carbon particles". In this complex mixture, one of the most intriguing forms is represented by the carbon onions, namely, large concentric (multi-shell) fullerenes.[1,2] Thus far, these interesting and uniquely structured forms have been studied for their tribological properties and for their potential presence in the interstellar dust.[3]

Here we report, for the first time, a method for chemically functionalizing onions from arc discharge soots. The new methodology not only allows the isolation of giant fullerenes, but especially renders them soluble in organic solvents, such that their solution properties can be studied for the first time.

The raw soot, as obtained from Bucky-USA, Houston, TX (Bu-202), is generated by arc discharge. A quantity of this material (50 mg) was suspended in 50 mL of toluene. Amino acid **1** (100 mg) and paraformaldehyde (200 mg) were added, and the resulting mixture was refluxed for 4 days (Scheme 1).

The conditions are similar, but not identical, to those reported recently for the organic functionalization of carbon nanotubes.[4] The difference lies in solvent: toluene does not disperse the nanotubes as well as DMF; therefore, only small particles will solubilize and react. After cooling, the toluene phase was separated by filtration, and the solid was washed several times by toluene and finally suspended in 100 mL of chloroform. After one week, a solid was formed, which TEM showed to be mostly amorphous carbon (Figures S1 and S2, Supporting Information). The precipitate was removed, leaving a green-black transparent solution, which, upon evaporation, afforded 7 mg of a black solid. The final product **2** was soluble in many organic solvents, especially chloroform and dichloromethane, with a solubility of about 10 and 7 mg per 100 mL, respectively. In these solvents, the solution was stable for at least two weeks, after which time some precipitate started to occur. However, the solid was readily resolubilized with 5 min of sonication in a water bath. A more dilute solution (<5 mg/100 mL) was stable indefinitely without causing any noticeable precipitation.

The proton NMR spectrum of **2** in deuteriochloroform shows a series of broad signals between 3 and 4 ppm, attributed to the oligoethylene chain and, tentatively, to the pyrrolidine protons (Figure S3, Supporting Information). The peaks appear broad because of the different local magnetic environments experienced by each single addend.

Elemental analysis and MALDI mass spectrometry give further information on the presence of the aliphatic chains (see Supporting Information).

As shown in Figure 1 (TEM images), the functionalized onions **2** consist of concentric shells and have diameters between 60 and
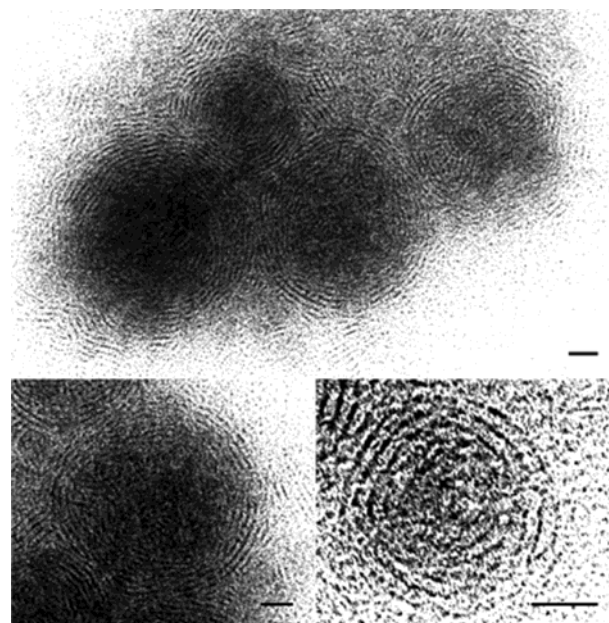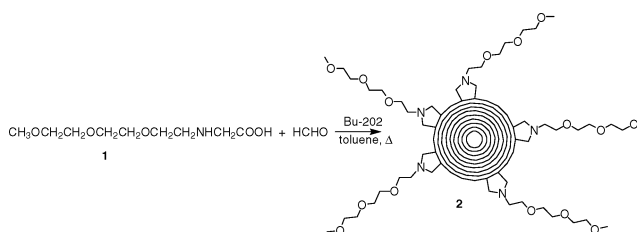

Figure 1. TEM micrographs of onions **2**. Bars represent 20 nm.

Scheme 1. Functionalization of Carbon Onions

300 nm, while the space between the internal shells has a mean value of ca. 4 nm. TEM analysis shows that the solid that did not dissolve in chloroform (see above) consists mainly of amorphous carbon. This indicates that it is possible to purify onions from amorphous carbon.

The UV−vis spectrum shows a series of transitions in the UV region with maxima at 230 and 265 nm due to π-plasmons of sp^2-like carbon atoms (Figure 2). Similar bands have recently been attributed to carbon onions (peak centered at 225 nm) and graphitic residues (265 nm).[3] The absorption decreases in the visible and near-infrared regions, but the functionalized onions still absorb at 2000 nm. Upon excitation with a 380 nm wavelength, a rather broad emission was detected with a maximum at 450 nm. In reference to 9,10-diphenylanthracene, the fluorescence quantum yield was determined to be 0.08%. Quite interestingly, variation of the excitation wavelength between 300 and 460 nm led to a shift of the emission maximum from 395 to 515 nm, respectively. The shift can be rationalized by assuming excitation of distinct carbon shells

† Università di Trieste.
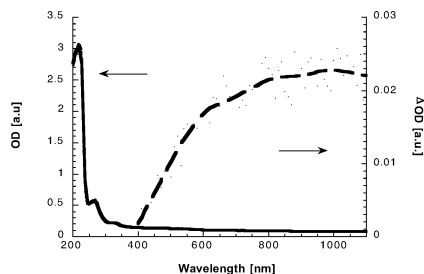‡ University of Notre Dame.
§ Università di Padova.

Figure 2. UV−vis−NIR spectra of onions **2**. Ground state (solid line); excited state (dashed line).

and/or carbon onions of different sizes. Also, the emission lifetime changed similarly. The emission time profiles, recorded at different wavelengths between 350 and 550 nm, cannot be fitted by a single exponential decay. Instead, a multiexponential fit was applied in which the major component gave rise to an interesting trend. The emission in the low-energy region exhibits appreciably longer lifetimes (550 nm; 3.13 ns) than the corresponding ones at shorter wavelengths (400 nm; 1.85 ns).

In time-resolved transient absorption measurements following an 8-ns short 337-nm laser pulse, the instantaneous formation of a broad transient was recorded, which covers most of the visible and near-infrared region (Figure 2). Similar transients were found upon excitation at 308, 355, or 532 nm. Implicit in this picture is that this newly formed species is a triplet excited state, product of an efficient intersystem crossing (i.e., low fluorescence quantum yields). An oxygen-sensitive lifetime of up to 105 ns further supports the triplet assignment. However, considering the fact that inner shells, which are well-isolated from oxygen in the solvent environment, are very likely excited, the rate constant with oxygen ($1.6 \times 10^9 \, M^{-1} \, s^{-1}$) implies a good coupling between the various spheres. Using the comparative method, we determined an absorption coefficient of 55 000 $M^{-1} \, cm^{-1}$ at 950 nm.

The strong difference of absorption coefficient between the ground and excited state is indicative of a potential broad-band optical limiter. Self-activated or photoactivated filters, usually called optical limiters, are triggered by the incident light and are a most promising way to protect sensors against pulsed laser light.[5] The basic mechanism of action is of a molecular type, one of the possible ways being the reverse saturable absorption (RSA), so-called in opposition to saturable absorption (SA). RSA usually occurs for molecules that, at the operating wavelengths, have excited-state absorption cross sections much larger than the ground-state ones.

Besides fullerenes[6] and fullerene derivatives,[7] other carbon materials occupy a leading position, although their optical limiting (OL) behavior stems from different microscopic mechanisms. Carbon black suspensions (CBS), single-walled nanotubes (SWNT) and multiwalled nanotubes (MWNT) are representative examples of this variety. In contrast to the case of fullerenes, for which RSA has been demonstrated, nonlinear scattering induced by optical breakdown is believed to be the dominant mechanisms for OL in CBS[8] and NT.[9]

Indeed, a solution of functionalized onions **2** in chloroform (0.5 mg in 5 mL) does show excellent optical limiting behavior, both at 532 and 1064 nm (Figure S4, Supporting Information). A useful figure of merit for optical limiting is the ratio (FOM = T_{lin}/T_{NL}) between the linear transmittance and the nonlinear transmittance

at the maximum input energy. The maximum possible value of FOM for a solution sample of length L and a molar concentration C of molecules with triplet and ground-state extinction coefficients ϵ_T and ϵ_G, respectively, is $FOM_{max} \approx \exp[(\epsilon_T - \epsilon_G)CL]$ and is attained if the input energy is high enough to transfer all the molecules to the excited state. In the functionalized onions the difference $(\epsilon_T - \epsilon_G)$ is a broad, increasing function of wavelength in the visible and near-infrared region of the spectrum up to 1000 nm. FOM values of 20 and 40 were measured for onions **2** at 532 and 1064 nm with maximum energies of 1.8 and 6 mJ, respectively. The observed behavior can be understood on account of the increasing difference between ground- and excited-state absorption coefficients on moving toward the infrared, while optical pumping into the triplet continues to be possible because of the weak extended ground-state absorption. To assess the performance in the visible, the OL behavior of the solution of **2** at 532 nm has been compared with the OL behavior of a typical fulleropyrrolidine (FULP) derivative in toluene solution at 690 nm where FULP exhibits best performance.[7] Already at 532 nm, the FOM value of **2** is almost the same as that of FULP at 690 nm, showing that **2** is a good optical limiter also in the green. The performance of **2** further increases in going from 532 to 1064 nm. By considering the ground state and the transient excited-state spectrum, it is possible to conclude that in **2** the OL is largely due to absorptive processes. Thus, the functionalized onions appear as good candidates for optical-limiting applications extending from the visible to the NIR.

In conclusion, we report for the first time the organic functionalization of carbon onions. Their nonlinear optical properties have been studied in solution for application as broad-band optical limiters. It was found that the functionalized onions are an example of soluble material that functions equally well in both the visible and the NIR regions.

Supporting Information Available: Experimental details pertaining to the preparation and properties of functionalized onions **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Iijima, S. *J. Cryst. Growth* **1980**, *50*, 675−683.
(2) Ugarte, D. *Nature* **1992**, *359*, 707−709.
(3) Calbioc'h, T.; Thune, E.; Rivière, J.; Camelio, S.; Girard, J.; Guérin, P.; Henrard, L.; Lambin, P. *J. Appl. Phys.* **2002**, *91*, 1560−1567.
(4) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760−761.
(5) *Power-Limiting Materials and Devices*, Proceedings of SPIE, Denver, CO, July 21−22, 1999; Lawson, C. M., Ed.; Society of Photo-Optical Instrumentation Engineers: Bellingham, WA, 1999; Vol. 3798.
(6) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225−226.
(7) Signorini, R.; Zerbetto, M.; Meneghetti, M.; Bozio, R.; Maggini, M.; De Faveri, C.; Prato, M.; Scorrano, G. *Chem. Commun.* **1996**, 1891−1892.
(8) (a) Mansour, K.; Soileau, M. J.; Van Stryland, E. W. *J. Opt. Soc. Am. B* **1992**, *9*, 1100−1109. (b) Nashold, K. M.; Walter, D. P. *J. Opt. Soc. Am. B* **1995**, *12*, 1228−1237.
(9) (a) Riggs, J.; Walker, D.; Carroll, D.; Sun, Y.-P. *J. Phys. Chem. B* **2000**, *104*, 7071−7076. (b) Vivien, L.; Riehl, D.; Lancon, P.; Hache, F.; Anglaret, E. *Opt. Lett.* **2001**, *26*, 223−225.

JA0342805