

# American Chemical Society

## National Awards Nomination Packet

### ACS Award for Creative Work in Fluorine Chemistry:2018 for: Olga Boltalina

Received: 09/26/2016

Cycle Year: 1

*"For the synthesis, characterization, and applications of fluorofullerenes, compounds of C60 and higher fullerenes with F atom substituents"*

#### **NOMINATOR:**

Alain Tressaud  
Icmcb-CNRS  
87 Ave Dr A Schweitzer  
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France

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- Have you discussed this award nomination with the nominee? No

#### **NOMINEE:**

Olga Boltalina  
2061 Stoney Hill Ct  
Fort Collins, CO 80525-1293  
UNITED STATES

Tel: (970)227-1756  
Email: olga.boltalina@colostate.eduXXX

ACS Current Member: Yes  
Years of Service: 12  
Present Position: Senior Research Associate,  
Department of Chemistry,  
Colorado State University, Fort  
Collins, CO,  
Industry: Academia

#### **CODE OF CONDUCT:**

- To the best of my knowledge, including past and present circumstances, the nominee:
  1. Employs and requires good safety protocols and practices in his/her laboratory and/or work environment;
  2. Upholds the highest ethical standards in his/her laboratory and/or work environment; and
  3. Otherwise engages in conduct that is consistent with both the objects of the American Chemical Society as stated in Article II Section 1 of its Constitution and the Chemical Professional Code of Conduct.

Code of Conduct Answer: Yes

#### **SUPPORTER 1**

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**Alain TRESSAUD**

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Bordeaux, Sept.12, 2016

***Ref - Nomination of Olga Boltalina for the 2018 ACS Award for Creative Work in Fluorine Chemistry***

Dear Award Committee,

I nominate Olga Boltalina for the 2018 ACS Award for Creative Work in Fluorine Chemistry: *For the synthesis, characterization, and applications of fluorofullerenes, compounds of C<sub>60</sub> and higher fullerenes with F atom substituents.* Boltalina deserves this award for her seminal, voluminous, and imaginative research on fullerene-(F)<sub>n</sub> compounds.

The beginning of fluorofullerene chemistry (1991-1993) was fraught with reports of complex, poorly-characterized C<sub>60</sub>F<sub>n</sub> reaction mixtures. A few papers even announced the synthesis of the putative molecule C<sub>60</sub>F<sub>60</sub>, which has never been confirmed. Boltalina literally took over the field in 1994. Since that time, she has been, and still is, the undisputed master synthetic chemist who prepared and studied dozens of highly-purified single-isomer fluorofullerenes, many of which have unprecedented structures and unique properties. Her original and innovative one-step, high-yield synthesis of D<sub>3</sub>-C<sub>60</sub>F<sub>48</sub> is the preferred method for making this important compound. (In contrast, Gakh's method requires three steps, a NaF matrix, and results in lower purity and a lower yield.)

The following is the quintessential example of Boltalina's creative approach to fluorine chemistry. She studied high-temperature reactions of fullerenes with high-valent metal fluorides under dynamic vacuum conditions inside a mass spectrometer. The MF<sub>n</sub> reagent decomposed to lower-valent MF<sub>n-1</sub> and F atoms at a particular temperature, and the F atoms added to the fullerene. By varying the MF<sub>n</sub> reagent, temperature, rate of heating, pressure, and the fullerene, one or more volatile fluorofullerenes sublimed out of the hot zone and were detected as negative ions in the mass spectrometer. Dozens of sets of reaction conditions could be readily studied using what were then exotic fullerenes only available in sub-milligram amounts. When larger amounts of fullerenes became available, Boltalina was ready with the right conditions to produce what became "her" unique fluorofullerene derivatives in macroscopic amounts and in high compositional and isomeric purity. This clever and imaginative work is widely recognized as a synthetic "tour de force".

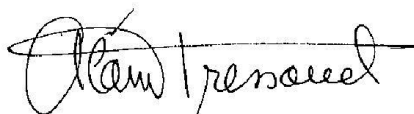
Boltalina prepared and characterized "Saturn-shaped" C<sub>60</sub>F<sub>20</sub>. There are millions of possible C<sub>60</sub>F<sub>20</sub> isomers, not to mention many other compositions with from 2 to 48 F atoms. After screening 12 fluorinating agents from KCrF<sub>4</sub> to Cs<sub>2</sub>CuF<sub>6</sub> and dozens of reaction conditions, Boltalina was able to isolate significant amounts of "Saturnene," D<sub>5d</sub>-C<sub>60</sub>F<sub>20</sub>. There are 8 peer-review articles about this compound, and she is the senior author of 6 of them.

Although Saturnene is a laboratory curiosity, Boltalina developed synthetic procedures for highly-pure gram quantities of fluorofullerenes that became materials of importance for a variety of applications being pursued by other scientists and engineers. The most important of these are  $C_{3v}$ - $C_{60}F_{18}$ ,  $C_{60}F_{36}$  (3 isomers), and, as discussed above,  $D_3$ - $C_{60}F_{48}$ . One or more of them is a topic in 238 peer-review articles published between 1994 and mid-2016. Boltalina is a co-author on 81 of them. Her collaborators Taylor, Sidorov, Strauss, and Seppelt are co-authors on only 55, 36, 9, and 6 of them (no one else has more than 27, and no one outside the four laboratories in which she personally pursued her chemistry with her own hands, in Moscow, Sussex, Berlin, and Fort Collins, has more than 10). She is the principal investigator among all of her co-workers and collaborators. These figures also speak to the impact of her work: more than 500 scientists and engineers around the world other than Boltalina have written 157 papers using or discussing these compounds. Furthermore, Boltalina's 81 papers on these compounds have been cited in more than 600 separate peer-review papers by others.

Boltalina also pioneered creative synthetic methods to make fluorofullerenes that could not be prepared simply by adding F atoms to underivatized fullerenes. For example, the high-symmetry molecule  $T_h$ - $C_{60}Br_{24}$  is made from  $C_{60}$  and  $Br_2$ , but no fluorinating agent produces any  $C_{60}F_{24}$  isomer. Undaunted, she reacted  $T_h$ - $C_{60}Br_{24}$  with  $XeF_2$  in anhydrous HF at 25 °C and produced isostructural  $T_h$ - $C_{60}F_{24}$  in good yield. After HPLC purification, its single-line  $^{19}F$  NMR spectrum confirmed its structure, making it the first fluorofullerene with a non-contiguous addition pattern of F atoms. DFT calculations showed that this isomer is 300 kJ mol<sup>-1</sup> less stable than alternative structures with 24 contiguous C-F vertexes.

In summary, Olga Boltalina's extensive, creative, and important work on fluorofullerenes makes her extremely well-deserving of the 2018 ACS Award for Creative Work in Fluorine Chemistry.

Sincerely,



Alain Tressaud  
2011 - ACS Award for Creative Work in Fluorine Chemistry

## **Olga V. Boltalina**

Department of Chemistry, Colorado State University (CSU), Fort Collins, CO 80523 USA  
970-227-1756 voice 970-491-1801 fax olga.boltalina@colostate.edu

### **PERSONAL**

Born March 10, 1960, in Kiev, USSR.  
Married to Dr. Steven H. Strauss (February 2002).  
Citizen of the Russian Federation and the United States of America.

### **EDUCATION**

M.S., Chemistry (cum laude), Moscow State University (MSU), Moscow, Russia, 1982.  
Ph.D., Physical Chemistry, MSU, Moscow, Russia, 1990.  
D.Sc. (Doctor of Science (Habilitation)), Physical Chemistry, MSU, Moscow, Russia, 1998.

### **PROFESSIONAL POSITIONS**

Junior Research Chemist, Moscow State University (MSU), Moscow, Russia, 1982–1990.  
Senior Research Scientist, MSU, Moscow, Russia, 1990–1998.  
Lead Scientist, MSU, Moscow, Russia, 1998–2003.  
Professor of Physical Chemistry, MSU, Moscow, Russia, 2003–2005; retired.  
Senior Research Associate, Colorado State Univ., Fort Collins, CO, 2002–present.  
Research Scholar III, Colorado State Univ., Fort Collins, CO, 2013–present.

### **PUBLICATIONS**

Principal author of more than 250 publications in peer-review journals and monographs.  
Principal inventor of more than 10 U.S. and Russian patents and patent applications.

### **PROFESSIONAL ACTIVITIES**

Present or past consultant on fluorine chemistry for five chemical technology companies.  
Member, Electrochemical Society (ECS), 1997–present.  
ECS Nanocarbons Division Executive Committee, 1997–present.  
Organizer/Co-organizer of eleven (11) symposia at ECS National Meetings, 1998–2009.  
Advisory Board, *Fullerene Science & Technology*, 2000–present.  
Member, ACS Division of Fluorine Chemistry, 2001–present.  
Int'l. Advisory Board, European Symposium on Fluorine Chemistry, 2005–2015.  
International Steering Committee on Fluorine Chemistry, 2007–present.  
Chair, ECS Smalley Award Selection Committee, 2008–2009.  
Program Chair, 19<sup>th</sup> Int'l. Symposium on Fluorine Chemistry, Jackson Hole, WY, 2009.  
Secretary, ECS Nanocarbons Division, 2016–2018.

### **HONORS AND AWARDS**

Royal Society Research Fellowship, UK, 1994.  
Visiting Scientist, Inst. of Physics & Astronomy, Aarhus Univ., Denmark, 1994 and 1998.  
Royal Society International Author Award, UK, 1996 and 2000.

(continued on next page)

**HONORS AND AWARDS** (continued)

President of Russia Award for Young Doctors of Science, 1998–2001.

JSPS Visiting Scholar, Shinshu University, Nagano, Japan, 1998.

Moscow State University Shuvalov Prize, Russia, 2000.

Moscow State University Lomonosov Prize, Russia, 2003.

Humboldt Foundation Friedrich Bessel Award, Germany, 2003–2004.

Humboldt Foundation Research Award, Germany, 2009–2010.

**RESEARCH INTERESTS**

Synthetic fluorine chemistry of fullerenes and other carbon allotropes, transition metal fluorides, mass spectrometry, gas-phase ion thermochemistry, and the application of fluorinated materials in molecular electronics, materials science, nanoscience, nanotechnology.

**Olga V. Boltalina — List of 20 Most Important Papers in Fluorine Chemistry**

1. **Boltalina, O. V.**; Borschevskii, A. Y.; Sidorov, L. N.; Street, J. M.; Taylor, R. "Preparation of  $C_{60}F_{36}$  and  $C_{70}F_{36/38/40}$ ," *Chem. Commun.* **1996**, 529–530.
2. **Boltalina, O. V.**; Markov, V. Y.; Taylor, R.; Waugh, M. P. "Preparation and characterisation of  $C_{60}F_{18}$ ," *Chem. Commun.* **1996**, 2549–2550.
3. Bagryantsev, V. F.; Zapol'skii, A. S.; **Boltalina, O. V.**; Galeva, N. A.; Sidorov, L. N. "Synthesis of  $C_{60}F_{48}$  in the reaction of  $C_{60}$  with molecular fluorine," *Doklady Akademii Nauk* **1997**, 357, 487–489 (English translation).
4. **Boltalina, O. V.**; Street, J. M.; Taylor, R. " $C_{60}F_{36}$  consists of two isomers having  $T$  and  $C_3$  symmetry," *J. Chem. Soc. Perkin Trans. 2* **1998**, 649–653.
5. **Boltalina, O. V.**; Street, J. M.; Taylor, R. "Formation of triumphene,  $C_{60}F_{15}Ph_3$ : first member of a new trefoil-shaped class of phenylated 60 fullerenes," *Chem. Commun.* **1998**, 1827–1828.
6. **Boltalina, O. V.**; Avakyan, T. V.; Markov, V. Y.; Dennis, T. J. S.; Abdul-Sada, A. K.; Taylor, R. "Formation of  $C_{76}F_{38}$ ,  $C_{78}F_{38}$ ,  $C_{82}F_{44}$ ,  $C_{84}F_{40}$ , and  $C_{84}F_{44}$ ," *J. Phys. Chem. B* **1999**, 103, 8189–8191.
7. **Boltalina, O. V.**; Markov, V. Y.; Borschevskii, A. Y.; Galeva, N. A.; Sidorov, L. N.; Gigli, G.; Balducci, G. "Saturated vapor pressure and sublimation enthalpy of fluorine derivatives of  $C_{60}$ ," *J. Phys. Chem. B* **1999**, 103, 3828–3832.
8. **Boltalina, O. V.**; Lukonin, A. Y.; Street, J. M.; Taylor, R. " $C_{60}F_2$  exists!," *Chem. Commun.* **2000**, 1601–1602.
9. Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; **Boltalina, O. V.**; Lukonin, A. Y.; Sidorov, L. N. "Enthalpy of formation and C–F bond enthalpy of fluorofullerene  $C_{60}F_{36}$ ," *J. Phys. Chem. B* **2000**, 104, 5403–5405.
10. Neretin, I. S.; Lyssenko, K. A.; Antipin, M. Y.; Slovokhotov, Y. L.; **Boltalina, O. V.**; Troshin, P. A.; Lukonin, A. Y.; Sidorov, L. N.; Taylor, R. " $C_{60}F_{18}$ , a flattened fullerene: Alias a hexa-substituted benzene," *Angew. Chem. Int. Ed.* **2000**, 39, 3273–3276.
11. Goryunkov, A. A.; Markov, V. Y.; **Boltalina, O. V.**; Zemva, B.; Abdul-Sada, A. K.; Taylor, R. "Reaction of silver(I) and (II) fluorides with  $C_{60}$ : thermodynamic control over fluorination level," *J. Fluorine Chem.* **2001**, 112, 191–196.
12. Troyanov, S. I.; Troshin, P. A.; **Boltalina, O. V.**; Ioffe, I. N.; Sidorov, L. N.; Kemnitz, E. "Two isomers of  $C_{60}F_{48}$ : An indented fullerene," *Angew. Chem. Int. Ed.* **2001**, 40, 2285–2287.

13. **Boltalina, O. V.**; Goryunkov, A. A.; Markov, V. Y.; Ioffe, I. N.; Sidorov, L. N. "In situ synthesis and characterization of fullerene derivatives by Knudsen-cell mass spectrometry," *Int. J. Mass Spectrom.* **2003**, 228, 807–824.
14. Goryunkov, A. A.; Markov, V. Y.; Ioffe, I. N.; Bolskar, R. D.; Diener, M. D.; Kuvychko, I. V.; Strauss, S. H.; **Boltalina, O. V.** " $C_{74}F_{38}$ : An exohedral derivative of a small-bandgap fullerene with  $D_3$  symmetry," *Angew. Chem. Int. Ed.* **2004**, 43, 997–1000.
15. Denisenko, N. I.; Troyanov, S. I.; Popov, A. A.; Kuvychko, I. V.; Zemva, B.; Kemnitz, E.; Strauss, S. H.; **Boltalina, O. V.** " $T_h$ - $C_{60}F_{24}$ ," *J. Amer. Chem. Soc.* **2004**, 126, 1618–1619.
16. **Boltalina, O. V.**; Streletskii, A. V.; Ioffe, I. N.; Hvelplund, P.; Liu, B.; Nielsen, S. B.; Tomita, S. "Formation of long-lived fluorofullerene trianions in collisions with Na," *J. Chem. Phys.* **2005**, 122, 021102(1–3).
17. Streletskii, A. V.; Ioffe, I. N.; Kotsiris, S. G.; Barrow, M. P.; Drewello, T.; Strauss, S. H.; **Boltalina, O. V.** "In-plume thermodynamics of the MALDI generation of fluorofullerene anions," *J. Phys. Chem. A* **2005**, 109, 714–719.
18. Strobel, P.; Riedel, M.; Ristein, J.; Ley, L.; **Boltalina, O. V.** "Surface transfer doping of diamond by fullerene," *Diamond Related Mater.* **2005**, 14, 451–458.
19. Wang, X.-B.; Chi, C.; Zhou, M.; Kuvychko, I. V.; Seppelt, K.; Popov, A. A.; Strauss, S. H.; **Boltalina, O. V.**; Wang, L.-S. "Photoelectron Spectroscopy of  $C_{60}F_n^-$  and  $C_{60}F_m^{2-}$  ( $n = 17, 33, 35, 43, 45, 47$ ;  $m = 34, 46$ ) in the Gas Phase and the Generation and Characterization of  $C_{60}F_{47}^-$  and  $D_2$ - $C_{60}F_{44}$  in Solution," *J. Phys. Chem. A*, **2010**, 114, 1756–1765.
20. Ibrahim, I.; Bachmatiuk, A.; Rummeli, M. H.; Wolff, U.; Popov, A.; **Boltalina, O. V.**; Buchner, B.; Cuniberti, G. "Growth of catalyst-assisted and catalyst-free horizontally aligned single wall carbon nanotubes," *Physica Status Solidi B* **2011**, 248, 2467–2470.

*The University of Texas at El Paso*



Luis A. Echegoyen  
Robert A. Welch Professor  
Department of Chemistry

August 29, 2016

ACS Awards Committee

**Re: Nomination of Olga Boltalina for 2018 ACS Award for Creative Work in Fluorine Chemistry**

Dear Award Committee,

I strongly second the nomination of Olga Boltalina for the 2018 ACS Award for Creative Work in Fluorine Chemistry: *For the synthesis, characterization, and applications of fluorofullerenes*. Others will write about Boltalina's fluorine-chemistry creativity and her impact on fluorine chemistry specifically. I will highlight the impact her research has had on chemistry more broadly, especially the chemistry of carbon allotropes. In addition to her ACS and international fluorine-chemistry community service, Boltalina served on the Electrochemical Society (ECS) Nanocarbons Division Executive Committee (1997-present). She also organized 11 fullerene symposia at ECS national meetings. Lecturing on fluorofullerenes at these and other ECS and international nanocarbon meetings, Boltalina brought her creativity and knowledge of fluorine chemistry to chemists and physicists *outside* the fluorine-chemistry community, encouraging and enabling them to use F-atom substituents for carbon nanotubes, nanohorns, etc., in their own research.

Boltalina discovered that small-bandgap and poorly-characterized  $C_{74}$  has an electron affinity higher than  $C_{60}$ ,  $C_{70}$ , and  $C_{76}$ . She then produced  $C_{74}F_2$  in her Knudsen-cell mass spectrometer and determined that no other fullerene has a stronger fluorine affinity than  $C_{74}$ . She realized that chemical functionalization of  $C_{74}$  widens the bandgap and makes  $C_{74}F_n$  derivatives stable and isolable, and this led to her remarkable selective synthesis of  $D_3-C_{74}F_{38}$ , the first exohedral derivative of  $C_{74}$ .

Over the years Boltalina prepared, developed ingenious chromatographic methods for, and characterized 14  $C_{60}F_n$  derivatives. This work *experimentally* demonstrated two important trends in small-substituent additions to fullerenes that had only been theoretically predicted previously: (i) contiguous addition patterns and (ii) the stabilizing effect of isolated benzenoid rings. It is significant that the  $C_{3v}$  structure of  $C_{60}H_{18}$ , which was reported *before* Boltalina's  $C_{60}F_{18}$ , was



only determined by X-ray diffraction 15 years *after* Botalina reported the X-ray structure of  $C_{3v}$ - $C_{60}F_{18}$ .

Botalina has completely dominated fluorofullerene chemistry since the start of her independent career. From 1994-2001 (before moving to Fort Collins), 61 peer-review articles on  $C_{60}F_{18}$ ,  $C_{60}F_{20}$ ,  $C_{60}F_{36}$ , and/or  $C_{60}F_{48}$  were published. Botalina authored 37 of these papers. The next highest number is for her Sussex collaborator Taylor (22, all but 5 of them with Botalina). She has always been the primary driving force behind the synthesis and characterization of fluorofullerenes, which she and many others are now using for applications ranging from OPVs to OFETs to the surface modification of diamond. This is exceptionally significant and creative work, and she is truly deserving of this award.

Sincerely,

A handwritten signature in blue ink, reading "Luis Echegoyen". The signature is fluid and cursive, with a long horizontal stroke extending from the end.

Dr. Luis Echegoyen  
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## POLITECNICO DI MILANO

DIPARTIMENTO DI CHIMICA, MATERIALI ED INGEGNERIA CHIMICA "Giulio NATTA"

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Milano, September 20, 2016

*To whom it may concern*

I the undersigned, Prof. Pierangelo Metrangolo, with this letter second the nomination of Olga Boltalina for the 2018 ACS Award for Creative Work in Fluorine Chemistry: *For the synthesis, characterization, and applications of fluorofullerenes, compounds of C<sub>60</sub> and higher fullerenes with F atom substituents*. Among the many important contributions of Boltalina's to fluorine chemistry, her creative and influential research on fluorofullerenes *alone* makes her worthy of this award. She combined her knowledge and expertise in mass spectrometry and fluorine chemistry to first identify and then prepare, isolate in macroscopic amounts, and study fluorofullerenes of C<sub>60</sub>, C<sub>70</sub>, C<sub>74</sub>, and C<sub>76</sub>–C<sub>84</sub>. She is the person most responsible for inventing and developing the field of fluorofullerene chemistry, the creative force and commander-in-chief of a team of Ph.D. student, co-workers, and chemist/physicist collaborators around the world.

The compound D<sub>2</sub>-C<sub>60</sub>F<sub>44</sub> exemplifies Boltalina's creativity. Work by others showed that reductive defluorination of C<sub>60</sub>F<sub>48</sub> with ferrocene or decamethylferrocene prior to injection into an ESI mass spectrometer produced a mixture of gas-phase species including C<sub>60</sub>F<sub>47</sub><sup>-</sup>, C<sub>60</sub>F<sub>45</sub><sup>-</sup>, C<sub>60</sub>F<sub>46</sub><sup>2-</sup>, and/or C<sub>60</sub>F<sub>46</sub><sup>2-</sup>, depending on the ferrocene used and its molar ratio. Boltalina cleverly used a lipophilic tetradecylferrocene with a reduction potential midway between ferrocene and decamethylferrocene that resulted in a soluble ferrocenium salt byproduct to cleanly produce, and subsequently characterize, D<sub>2</sub>-C<sub>60</sub>F<sub>44</sub> in solution (*J. Phys. Chem. A* **2010**). In this seminal paper, she invented the method of selective defluorination of a known fluorofullerene as a novel way to synthesize in high yield and purity an unknown fluorofullerene that cannot be prepared by fluorination alone.

In addition to the many C<sub>60</sub>F<sub>n</sub> compounds Boltalina has prepared and studied, she is the undisputed world leader in the selective fluorination of higher fullerenes. There are 28 experimental papers on C<sub>70</sub>F<sub>n</sub> compounds; she is a senior author on 10 (no one else has more than 9). There are 7 experimental papers on fluorinated derivatives of fullerenes from C<sub>74</sub> to C<sub>84</sub>, and Boltalina is a senior author on 6. Virtually all of the compounds she reported in these 6 papers required the development of non-obvious, creative methods of synthesis and purification. Virtually all of them have compositions and structures that were unprecedented in fullerene chemistry.

In summary, her fluorofullerene work has the significance and creativity that is the hallmark of every other fluorine chemist who has won this ACS award. She has my highest recommendation.

Sincerely yours

Sede Leonardo:

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