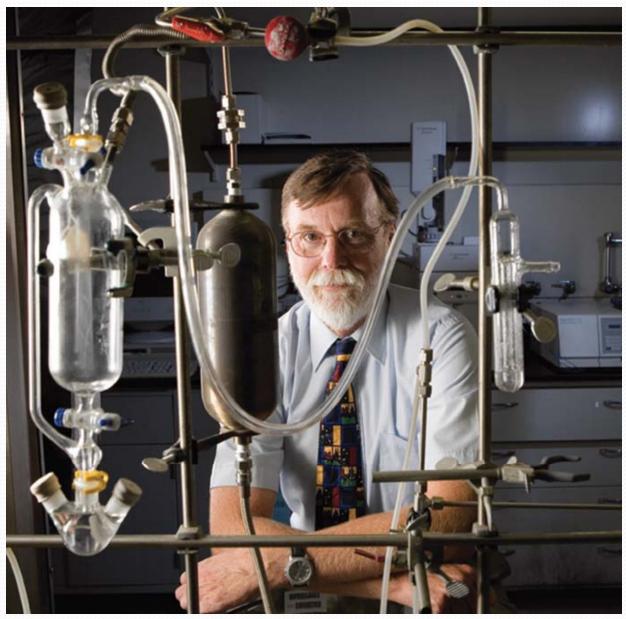
# Division of Fluorine Chemistry Spring 2008 Newsletter



**Dennis Curran** 2008 American Chemical Society Award for Creative Work in Fluorine Chemistry



About the cover

#### **Dennis Patrick Curran**

Dennis P. Curran received his B.S. in 1975 from Boston College. His Ph.D. was granted from the University of Rochester in 1979 where he worked under Professor Andrew S. Kende. After a two year postdoctoral stay with Professor Barry M. Trost at the University of Wisconsin, Dr. Curran joined the faculty of the Chemistry Department at the University of Pittsburgh in 1981. He now holds the ranks of Distinguished Service Professor and Bayer Professor of Chemistry, and is the founder of Fluorous Technologies, Inc. (www.fluorous.com). Among other awards, Dr. Curran has received the American Chemical Society Award for Creative Work in Fluorine Chemistry (2008), the University of Pittsburgh Innovator Award (2007), the Harry and Carol Mosher Award, Santa Clara Valley Section, ACS (2007), the Blaise Pascal International Research Chair, Préfecture de la Région D'Ile-de-France Paris (2007-2008), the Pittsburgh Award, Pittsburgh Section, American Chemical Society (2006), the Morley Medal, Cleveland Section, American Chemical Society (2006), the Pittsburgh Magazine Innovators Award (2003), American Chemical Society Award for Creativity in Organic Synthesis (2000) and the Cope Scholar Award (1988), and the Janssen Prize for Creativity in Organic Synthesis (1998). He is currently an ISI "Highly Cited Researcher" (www.isihighlycited.com). Dr. Curran has authored over 370 papers, thirty patents and two books, and is well known for his work in at the interface of radical chemistry and organic synthesis. More recently he has made significant contributions to the emerging discipline of fluorous chemistry. Additional information is at http://radical.chem.pitt.edu.



#### Message from the Chair

Greetings to all of my fluorine chemistry colleagues, from the Land of 10,000 Lakes! I welcome our newest members of the Executive Committee of the Division of Fluorine Chemistry. **Greg Butler** has joined us as our new Vice-Chair/Secretary, and **Paul Deck** and **Tariq Mahmood** are our newest at-large Executive Committee members. All of us on the Executive Committee thank outgoing members **Michael Gerken** and **Joseph Michl** for their service for the past three years. **Surya Prakash**, our most recent Division Chair, deserves special thanks for his excellent and highly effective contributions, both as Chair and as Vice-Chair/Programs, over the past four years.

The Division's program at the 235th National Meeting of the ACS in New Orleans, Louisiana (April 6-10, 2008), was outstanding for its quality and interest. A symposium (co-sponsored with the Division of Organic Chemistry) in honor of **Dennis Curran**, the recipient of the 2008 American Chemical Society Award for Creative Work in Fluorine Chemistry, was sponsored by SynQuest and organized by **Viacheslav Petrov** and **Surya Prakash**. Professor Curran's award address, *Fluorous Chemistry in Pittsburgh: 1994-2008*, highlighted important advances in and impacts of fluorous-phase chemistry, and many other areas of organofluorine chemistry were covered. A second symposium, *Fluorine in Drug Design* (co-sponsored with the Division of Medicinal Chemistry), sponsored by Air Products and organized by **James McCarthy**, added a great deal of interest from the medicinal chemistry point of view. The Division was also well-represented in the **Sci-Mix** poster session, organized by **Viacheslav Petrov**.

The Division (in conjunction with the Division of Polymer Chemistry) sponsored a symposium, *Fluorine-Containing Molecules and Polymers*, in honor of **Darryl DesMarteau**, at the 59<sup>th</sup> Southeastern Regional ACS (SERMACS) meeting in October of 2007. I was unable to attend, but by all accounts that I have heard, it was an excellent program. The symposium was organized by Dennis Smith and Joseph Thrasher.

Planning for the **19<sup>th</sup> Winter Fluorine Conference**, to be held in St. Pete Beach, Florida in January 2009, is well under way, and is titled *Fabulous Future with Fluorine*. The conference will, in addition to regular oral and poster sessions, have a special symposium titled *Fluorine in Medicines*, with presentations from researchers from the pharmaceuticals industry. The Award Address by the recipient of the 2009 ACS Award for Creative Work in Fluorine Chemistry will also be given. The organizers are P. V. Ramachandran (Chair) and Charles Martin (Co-Chair). The division will also host the **19<sup>th</sup> International Symposium on Fluorine Chemistry**, August 23-28, 2009 at Jackson Hole, Wyoming under the leadership of Joseph Thrasher, Olga Boltalina, Steven Strauss and Richard Fernandez.

The Annual General Business Meeting of the Division took place during the 235th National Meeting of the ACS April 2008 to approve the Treasurer's report and a slate of candidates for election to the Division's Executive Committee to be held next fall. I thank **Bob Syvret** for keeping the Division in a sound financial state.

The Fluorine Division is proud of the outcomes of its many years of sponsorship of the Moissan Summer Undergraduate Research Fellowships. These fellowships have been strong influences on the careers of many excellent young chemists who have interests in fluorine chemistry, and we know that the fellowships will continue to do so. The call for fellowships to be awarded in 2009 will appear in the Fall 2008 *Newsletter, Chemical and Engineering News*, and the *Journal of Fluorine Chemistry*.

The Moissan Fellowship faculty advisor awardees for this year are: **Alexander Doemling** (University of Pittsburgh), **Brian O'Brien** (Gustavus Adolphus College, Minnesota), and **John Welch** (State University of New York at Albany). I wish the student recipients of these stipends, along with their faculty advisors, great success in their summer research, and hope to see some of the research presented at the 19<sup>th</sup> Winter Fluorine Conference.

In order to maintain the current number of fellowships at the stipend level of \$3,500, we need to campaign strongly to increase the **Moissan Summer Undergraduate Research Fellowship in Fluorine Chemistry Fund**. I call upon individual members of the Division and corporate sponsors to support the drive to reach the goal of \$150,000 (see the Treasurer's Report for the most recent data). We intend to establish a self-sustaining investment pool (managed by the Fluorine Division) from which the Moissan Summer Undergraduate Fellowships can be funded. We hope that you and/or your organization will contribute to this important and highly successful outreach program of your Division and equally important investment in the future of fluorine chemistry. Contributions should be directed to the Fluorine Division's Treasurer, **Bob Syvret**. Please visit the Fluorine Division website for details.

The Fluorine Division website continues to be an exceedingly useful reference for matters pertaining to Fluorine Chemistry. We thank **Phil Henderson**, the site's Webmaster, for the considerable effort he has expended in maintaining the website. The website contains links to, among other items, past newsletters, annual reports to the ACS, listings of officers, membership information, safety information, upcoming meetings, programs, and Fluorine Division Bylaws, along with the Executive Committee Operations Manual. Suggestions for further useful additions to the website will be welcome.

Increasing the membership of the Division is a highly important priority. *I entreat each Division member to recruit at least one new member this year!* Membership application forms may be obtained from the Division's website. Please send completed membership forms to the Membership Chair, **Vadim Soloshonok**. *Remember, the first year of membership in the Division is free!* 

If there are concerns or questions that you have regarding the Fluorine Division, please send me an e-mail (bobrien@gustavus.edu). If there are items that you would like to have considered for inclusion in the *Newsletter*, or by the Executive Committee at its biannual meetings, please do the same.

The 2008 Fall ACS National Meeting in Philadelphia in August will feature several symposia in Fluorine Chemistry (see Program Chair's Report). I hope to see you there.

Brin a OBrie

Brian A. O'Brien Chair 2008



#### **Membership Chair's Report**

The Division had, as of March 1, 2008, 666 (total) members (Member - 597, Division Affiliate – 66, Society Affiliate - 3). We would like to thank all of you who promoted our Division and helped us to retain members and recruit new members. We welcome suggestions for activities that will help maintain and, most importantly, expand our membership.

We plan to publish and distribute a new membership directory later this year. If you wish to receive and have your name and contact information included in future Membership Directories, you will need to fill out an Opt-In Form (included in this newsletter, and also posted on the Fluorine Division's website). This needs to be done only once in a lifetime. If you wish to change or correct your contact information, please contact Vadim Soloshonok.

We request that every member actively recruit new members for the Division so as to achieve our goal of becoming a medium-size division. We would like to remind you that the first year of membership is free of charge, so please advise all your graduate students and colleagues who have an interest in Fluorine chemistry to enroll.

We welcome the following new members: Sebastian Hassenstab-Riedel (McMaster University), John Zimmerman (Henkel Technologies), Robert Simpson (Vitae Pharmaceuticals), Alexander Doemling (University of Pittsburg), Maryann C. Kenney (Saint Gobain), Philippe Bohlmann (University of Minnesota), Jin Montclare (Polytechnic University NY), Narayan Bhat (University of Texas), Ed Biehl (SMU), Alexey B. Dyatkin (Universal Display Corp.), H. R. Allcock (Pennsylvania State), Tony O'Lenick (Siltech), Rollie Sperber (Chemcollect, GmbH), Oliver Herd (Chemcollect, GmbH), Harald Ommer (Chemcollect, GmbH), Byron L. Bennett (Idaho State), Gang Qian (Pharmacopeia, Inc.), Ruth Ann Murphy (University of Mary Hardin-Baylor)



#### **Councilor's Report**

The ACS Council Meeting was held on Wednesday, April 9, 2008 in New Orleans, LA. Detailed below are some points of interest and information from the Council Meeting.

#### **Election Results**

The Committee on Nominations and Elections presented to the Council the following nominees for selection as candidates for President-Elect, 2009:

Thomas J. Barton, R. Stephen Berry, Joseph S. Francisco and Josef Michl. Each candidate presented a short oral presentation to the Council. By written ballot, the Council selected Joseph S. Francisco and Josef Michl as candidates for 2009 President-Elect. These two candidates will stand for election in the Fall National Election.

The Committee on Nominations and Elections announced the selection of the following candidates for Directors-at-Large for a 2009-2011 term: William F. Carroll, Jr., Richard L. Deming, Thomas R. Gilbert and Marinda Li Wu. The election of two Directors-at-Large will be conducted in the Fall (October).

#### Petitions

The Council received three amendments to the ACS ByLaws for action

1. The Council **voted** to approve the Petition on Election Procedures for President-Elect and District Director. The petition seeks to make the balloting procedure more uniform and to avoid complications and expense of run-off elections.

2. The Council, after a lively debate, **voted** to approve the Petition on Election Procedures (Part 2). This petition standardizes election processes for President-Elect and all Director positions based on percentages of voting members, and increases the number of required signatures (for petition candidates).

3. The Council **voted** to approve the Petition on Membership categories and requirements. This petition broadens qualifications for membership and creates a new category of student membership.

The Council **voted** to set the member dues for 2009 at the fully escalated rate of \$140.00.

This rate is established pursuant to an inflation-adjustment formula in the ACS Constitution and ByLaws.

#### **Society Finances**

The ACS ended 2007 with a net from operations of \$9.6 million, which was \$2.2 million favorable to the approved budget. This was based on total revenues of \$444.2 million and total expenses of \$434.6 million.

#### Attendance Report:

As of April 9, 2008, the ACS Spring Meeting had attracted 13,302 registrants as follows: regular attendees, 6,681; students 4,659; exhibitors, 1,156; exposition only, 374; and guests, 432.

#### **Revision of the Division Funding Formula**

The Council, after considerable discussion, **voted** to recommit the revised division funding formula, as presented by the Divisional Activities Committee, to the committee for further action at the fall national meeting.

#### **Member Statistics:**

At the close of 2007, Society membership totaled 160,052, despite a net loss of 439 members at the end of the year. Also, 2007 recorded the second highest number of new applications, 16,533.

#### Academic Professional Guidelines:

The Council voted to approve the Academic Professional Guidelines as submitted by the Committee on Economic and Professional Affairs. These guidelines apply to those members of the academic community whose job function impacts directly or indirectly on scientists practicing the profession of Chemistry.



#### **Treasurer's Report**

The fiscal state of the Division of Fluorine Chemistry continues to be very strong. The table below provides a snapshot view of the Division's assets as of 31 December 2007 and the comparative numbers for a year ago.

The Division's total assets increased moderately (5.2 %) over the course of the 12 months ending December 2007. This increase is primarily due to appreciation of invested funds; 5.0 % increase in Investment Pool and 6.2 % increase in Moissan SURF Fund.

#### Financial highlights for the Division for Fiscal Year 2007 include:

•In terms of the general operating account, expenses were greater than income by just \$78.21 indicating a relatively "flat" year financially.

•Actual income and expenses for 2007 were within 2% of budgeted values.

•The Division of Fluorine Chemistry continues to be committed to undergraduate research experience in fluorine chemistry. In 2007, the Division awarded three (3) Moissan Summer Undergraduate Research Fellowship awards of \$3,500 each to deserving undergraduate students interested in fluorine chemistry.

•The Division was the primary sponsor and provided financial support to the operation of the 18<sup>th</sup> Winter Fluorine Conference. Net proceeds were \$15,706.94 that went into the Division's operating account.

•The Division provided financial support (\$5,263.11) to speakers at the ACS National Meeting in Chicago participating in the Symposium to honor Professor Kenji Uneyama.

•The Division provided \$9,702 in sponsorship money for two Fluorine Division symposia held at the ACS National Meeting in Boston, August 2007.

•The Division provided \$2,500 in sponsorship money for a symposium in honor of Darryl DesMarteau that was held during the 2007 SERMACS meeting in Greenville S.C. October 24-27, 2007.

	(\$) as of 31 December 2006	(\$) as of 31 December 2007
ACS Investment Pool (market value)	129,692	136,132
Wachovia National Bank	8,584	8,506
American Express SPS Advantage Account		
Moissan SURF Fund	76,873	81,612
Total Assets	215,149	226,250
percent change		5.2%



#### **Program Chair's Report**

#### 235th ACS National Meeting

April 6-10, 2008, New Orleans, LA. Organizers: Professor G. K. S. Prakash and Dr. V. Petrov. As part of the 235<sup>th</sup> ACS meeting, the Fluorine Division held the ACS Award Symposium for Creative Work in Fluorine Chemistry in Honor of Professor Dennis Curran, the winner of the Award for 2008. Ten presentations were given during this interesting meeting. Talks delivered by an international array of scientists highlighted different areas of organofluorine chemistry. Professor D. Curran delivered a very interesting overview of the development of fluorous chemistry, titled "Fluorous Chemistry in Pittsburgh: 1994-2008. Five poster presentations were given at the Monday evening Sci-Mix poster session. The Division expresses gratitude to all speakers and organizers of the Symposium for putting together an excellent meeting.

#### **Upcoming Meetings**

#### 236th ACS National Meeting

August 17-21, 2008, Philadelphia, Pennsylvania Organizers:

David O'Hagan (do1@st-andrews.ac.uk)

Vadim Soloshonok (vadim@ou.edu)

Viacheslav Petrov (Viacheslav.A.Petrov@usa.dupont.com)

As part of 236<sup>th</sup> ACS meeting The Fluorine Division is organizing the Symposium "Fluorinated Biologically Active Compounds: Synthesis and Properties: Synthesis and Spectroscopy". This two and half day meeting will be held on August 17-19. The program is completed. It includes 32 invited and contributed talks and 5 poster presentations. Right now organizers are heavily involved in rising funds for the Symposium. Registration for 236<sup>th</sup> ACS meeting was open on May 1, 2008. More details on the program, registration and accommodations can be found at ACS website.

#### Fluoropolymer 2008. Current Frontiers and Future Trends

Dennis Smith (dwsmith@clemson.edu), Chair

The Division of Fluorine Chemistry is the co-sponsor of the meeting of "Fluoropolymer 2008. Current Frontiers and Future Trends" organized by ACS Division of Polymer Chemistry. This year, FLUOROPOLYMER 2008 will be held at the Doubletree Guest Suites in Historic Charleston, South Carolina, October 19-22, 2008. The deadline for abstract submission is August 1, 2008.

#### **19<sup>th</sup> Winter Fluorine Conference**

January 11-16, 2009, St Pete Beach, Florida Organizers:

P.V. Ramachandran (chandran@purdue.edu), Chair,

Charles Martin (cwmartin@wlgore.com), Co-Chair

Preparation for the meeting "Fabulous Future with Fluorine" is underway and organizers of the 19<sup>th</sup> Winter Fluorine Conference have been quite successful in raising funds for this meeting. The registration for 19<sup>th</sup> WFC starts on Monday, August 4 and will be open through December 11, 2008. The deadline for abstract submission is October 6, 2008. Visit the Fluorine Division website for further information (http://membership.acs.org/F/FLUO/).

#### 19th International Symposium on Fluorine Chemistry

August 23-28, 2009, Jackson Hole, Wyoming, USA Organizers:

Joseph Thrasher (fluorine@bama.ua.edu), Chair Olga Boltalina (olga.boltalina@colostate.edu), Co-Chair Steven Strauss (strauss@chem.colostate.edu), Co-Chair Richard Fernandez (fernanre@msn.com), Co-Chair

## Special Offer on Subscriptions to the Journal of Fluorine Chemistry for Members of the Division of Fluorine Chemistry

Members of the Division are normally offered a substantially discounted subscription rate for the *Journal of Fluorine Chemistry*. As of the time scheduled for printing and mailing of the newsletter, current subscription rates have not been received from the publisher, Elsevier. Please check the Division's website in the near future for an order form and current rates.



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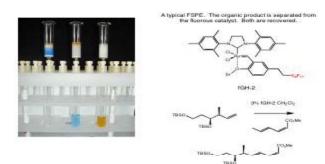
# Fluorous methods for synthesis of organic molecules

#### Dennis P. Curran

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Much current work in the field of fluorous chemistry relies on the use of fluorous stationary phases for separation. Following the introduction of fluorous tagging in 1996,<sup>1</sup> we soon introduced the technique of fluorous solid phase extraction (FSPE).<sup>2</sup> The FSPE separation (Figure 1) allows the use of smaller (and therefore lighter) fluorous tags, and the method is especially useful for small scale discovery chemistry and library applications in drug discovery and other areas.<sup>3</sup> A recent review of FSPE features almost one hundred papers that have used the technique.<sup>4</sup> Scores of light fluorous reagents, reactants, catalysts, scavengers and protecting groups are now commercially available from Aldrich, Waco and Fluorous Technologies, Inc.<sup>5</sup>

Figure 1. Fluorous Solid Phase Extraction: Separates tagged compounds (orange fraction) from untagged ones (blue fraction) by a generic filtration-like process



Our studies on FSPE soon led us to fluorous HPLC experiments, and this in turn led to the introduction of "fluorous mixture synthesis",<sup>6</sup> a technique that we have since used in many new guises. The underlying concepts behind fluorous mixture synthesis, Figure 2, are those of solution phase mixture synthesis with separation and identification tagging. Briefly, a series of substrates is tagged with a homologous series of fluorous tags. The resulting tagged substrates are mixed and then taken through a multistep synthesis to provide a mixture of tagged products. During this mixture synthesis phase, effort is saved proportional to the number of compounds that are mixed. Finally, the last mixture is demixed by fluorous HPLC to provide the individual tagged products, which are then detagged (deprotected) to provide the final target compounds The concepts of solution phase mixture synthesis are general, and Craig Wilcox introduced a new class of oligoethylene (OEG) tags.<sup>7</sup>

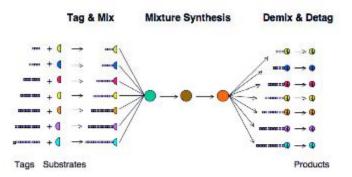
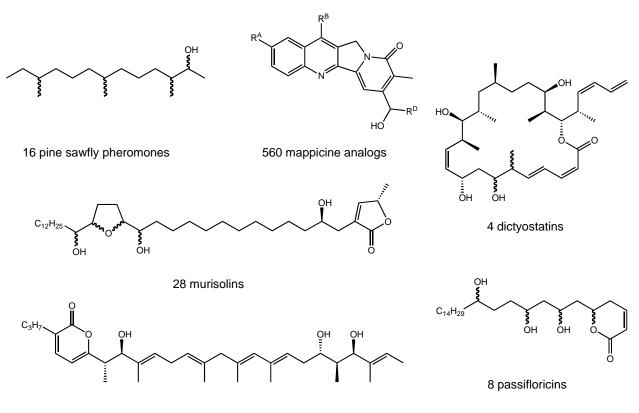


Figure 2. Concepts of Fluorous Mixture Synthesis: Substrates are tagged and mixed. Mixture synthesis then precedes demixing and detagging Soon after the introduction fluorous quasiracemic synthesis,<sup>8</sup>we introduced the concept of complete stereoisomer libraries<sup>[9</sup> (made by fluorous mixture synthesis), a concept that has been featured in much of our natural products work since then. We later united fluorous and OEG tags in the technique of double mixture synthesis. <sup>10</sup> These techniques have gone well beyond "proof-of-principle"; the derived products (see Figure 3) have been used to solve structure problems and provide importance biological information. <sup>11,12</sup>



4 lagunapyrones

Figure 3. Natural Products Made by FMS or Double Mixture Synthesis

All these applications are driven by the favorable features of fluorous tagging in reactions, identification and analysis, and separation. Most recently, these features have begun to be recognized by the chemical biology community, and a new wave of fluorous chemistry appears to be on the horizon.

I warmly thank an excellent cadre of collaborators and coworkers for their intellectual and experimental contributions as well as for their support and friendship. I thank the Institute of General Medical Sciences of the National Institutes of Health for sustained funding of our work in fluorous chemistry over more than a decade.

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### Fabulous Future with Fluorine

January **11-16**, 2009 TradeWinds Resorts and Conference Center St. Pete Beach, FL

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