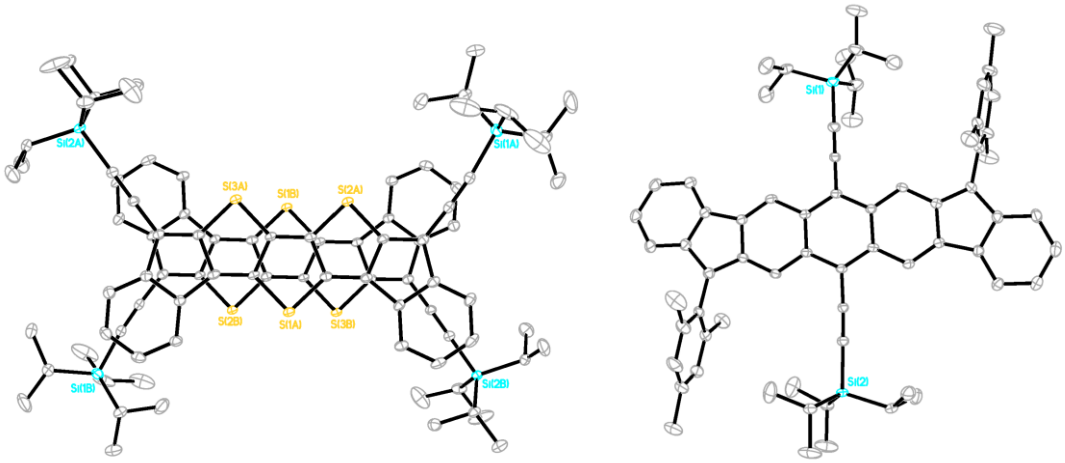
Indenofluorenes and Quinoidal Analogues – A New Class of Electron-Accepting Materials

Michael M. Haley

Department of Chemistry & Biochemistry and the Material Science Institute, University of Oregon, Eugene, Oregon 97403-1253, United States

This talk will present our synthetic, structural and materials studies of a new class of electron-accepting molecules based on the indenofluorene (IF) skeleton. The initial preparative route involved transannular cyclization of octadehydrodibenzo[12]annulenes to afford the pentacyclic ring system. Subsequent transformations generated the first stable examples of the fully conjugated, 20 pi-electron, formally anti-aromatic compounds.[1] Optimization of intermediate IF-6,12-dione synthesis via a simple three-step process now permits access to IF derivatives in multigram quantities.[2] Work on 6,12-diarylIFs demonstrated that single crystals of the pentafluorophenyl derivative could serve as an active layer in organic field effect transistors (OFETs) that exhibit ambipolar behavior using Au source/drain contacts.[3] Current studies are focused on varying the antiaromaticity of the indacene unit by replacement of the benzene groups with thiophene units[4] as well as increasing biradical character of the framework by expansion of the quinoidal core.[5]



[1] Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 1127.
[2] Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 11103.
[3] Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong, Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. *J. Am. Chem. Soc.* **2012**, *134*, 10349.
[4] (a) Young, B. S.; Chase, D. T.; Marshall, J. L.; Vonnegut, C. L.; Zakharov, L. N.; Haley, M. M. *Chem. Sci.* **2014**, *5*, 1008; (b) Marshall, J. L.; Uchida, K.; Frederickson, C. K.; Schütt, C.; Zeidell, A. M.; Goetz, K. P.; Finn, T. W.; Jarolimek, K.; Zakharov, L. N.; Risko, C.; Herges, R.; Jurchescu, O. D.; Haley, M. M., *Chem. Sci.* **2016**, *7*, 5547.
[5] (a) Rudebusch, G. E.; Fix, A. G.; Henthorn, H. A.; Vonnegut, C. L.; Zakharov, L. N.; Haley, M. M. *Chem. Sci.* **2014**, *5*, 3627; (b) Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce-Ortiz, R.; Gomez-Garcia, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. *Nature Chem.* **2016**, *8*, 753.

Michael M. Haley

Richard M. and Patricia H. Noyes Professor
Department of Chemistry & Biochemistry and the Materials Science Institute, University of Oregon
Address: 1253 Franklin Blvd, Eugene, Oregon 97403-1253, USA
Tel: +(1) 541-346-0456, Fax: +(1) 541-346-0487
E-mail: haley@uoregon.edu
Web: http://haleylab.uoregon.edu

[Degree] Ph. D., Rice University, 1991
[Professional Career] Assistant Professor, University of Oregon, 1993; Associate Professor, University of Oregon, 1999; Professor, University of Oregon, 2004; Department Head, 2008-2014; Richard M. and Patricia H. Noyes Professor, University of Oregon, 2013
[Research Fields] Organic chemistry; Materials chemistry; Supramolecular chemistry; Organic electronics
[Professional Society] American Chemical Society of Japan; Materials Research Society; American Association for the Advancement of Science
[Recent Honors] Fellow, American Association for the Advancement of Science, 2011; NSF Innovation Corps, "Best in Show" award, 2012; Alexander von Humboldt Research Fellowship, 2015; UO Research Excellence Award for Innovation and Impact, 2015; Japan Society for the Promotion of Science Fellowship for Research in Japan, 2016
[Recent Publications]

1) B. S. Young, D. T. Chase, J. L. Marshall, C. L. Vonnegut, L. N. Zakharov and M. M. Haley. "Synthesis and Properties of Fully-Conjugated Indacenedithiophenes." *Chem. Sci.* **2014**, *5*, 1008-1014.
2) B. D. Rose, N. J. Sumner, A. S. Filatov, S. J. Peters, L. N. Zakharov, M. A. Petrukhina and M. M. Haley. "Experimental & Computational Studies of the Neutral and Reduced States of Indeno[1,2-*b*]fluorene." *J. Am. Chem. Soc.* **2014**, *136*, 9181-9189.
3) G. E. Rudebusch, A. G. Fix, H. A. Henthorn, C. L. Vonnegut, L. N. Zakharov and M. M. Haley. "Quinoidal Diindenothienoacenes: Synthesis and Properties of New Functional Organic Materials." *Chem. Sci.* **2014**, *5*, 3627-3633.
4) C. L. Vonnegut, A. M. Shonkwiler, M. K. Khalifa, L. N. Zakharov, D. W. Johnson and M. M. Haley. "Facile Synthesis and Properties of 2-λ^5-Phosphaquinolines and 2-λ^5-Phosphaquinolinones." *Angew. Chem. Int. Ed.* **2015**, *54*, 13318-13322.
5) B. W. Tresca, R. J. Hansen, C. V. Chau, B. P. Hay, L. N. Zakharov, M. M. Haley and D. W. Johnson. "Substituent Effects in CH Hydrogen Bond Interactions: Linear Free Energy Relationships and Influence of Anions." *J. Am. Chem. Soc.* **2015**, *137*, 14959-14967.
6) G. E. Rudebusch, J. L. Zafra, K. Jorner, K. Fukuda, J. L. Marshall, I. Arrechea-Marcos, G. L. Espejo, R. Ponce-Ortiz, C. J. Gomez-Garcia, L. N. Zakharov, M. Nakano, H. Ottosson, J. Casado and M. M. Haley. "Diindeno-fusion of an Anthracene as a Design Strategy for Stable Organic Biradicals." *Nature Chem.* **2016**, *8*, 753-758.
7) G. E. Rudebusch, G. L. Espejo, J. L. Zafra, M. Peña-Alvarez, S. N. Spisak, K. Fukuda, Z. Wei, M. Nakano, M. A. Petrukhina, J. Casado and M. M. Haley. "A Biradical Balancing Act: Redox Amphoterism in a Diindenoanthracene Derivative Results from Quinoidal Acceptor and Aromatic Donor Motifs." *J. Am. Chem. Soc.* **2016**, *138*, 12648-12654.
8) C. K. Frederickson, L. N. Zakharov and M. M. Haley. "Modulating Paratropicity Strength in Diareno-Fused Antiaromatics." *J. Am. Chem. Soc.* **2016**, *138*, 16827-16838.