

Supplementary Information:

Discrimination of positional isomers by ion mobility mass spectrometry:

Application to organic semiconductors

Quentin Duez,^{a,b} Maxime Romain,^c Corentin Tonneaux,^{a,b} Julien De Winter,^a Vincent Lemaur,^b Jérôme Cornil,^{b*} Cyril Poriel,^{c*} and Pascal Gerbaux^{a*}

^a Organic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry (CISMa), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons - UMONS, 23 Place du Parc, 7000 Mons, Belgium

^b Laboratory for Chemistry of Novel Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons - UMONS, 23 Place du Parc, 7000 Mons, Belgium

^c Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France

* Corresponding author email: pascal.gerbaux@umons.ac.be (Ion mobility), jerome.cornil@umons.ac.be (Computational chemistry), cyril.poriel@univ-rennes1.fr (Synthesis)

Experimental

Synthesis

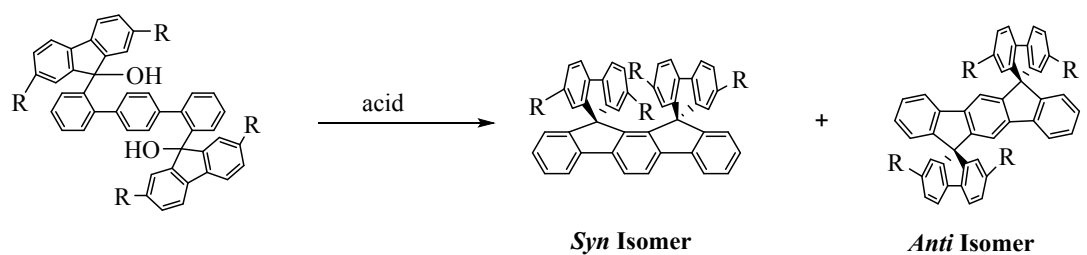
Synthetic procedures and full spectroscopic characterization of all the molecules investigated herein can be found in previous works:

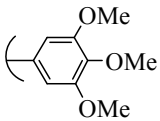
1a/1b in Ref [1]

2a/2b in Ref [2]

3a/3b in Ref [3]

4a/4b in Ref [4]



		<i>Syn Isomer</i>	<i>Anti Isomer</i>
R=	H	1a	1b
	<i>i</i> Bu	2a	2b
		3a	3b

Scheme S11: Synthesis of dihydroindenofluorene regioisomers

Ion Mobility Mass Spectrometry

IMMS experiments were performed using a Waters Synapt G2-Si mass spectrometer equipped with a Travelling Wave Ion Mobility Spectrometry (TWIMS) cell. Dihydroindenofluorene isomers solutions were prepared at a concentration of 1mM in dichloromethane and diluted to 10 μ M with acetonitrile. These diluted solutions were infused in the instrument ElectroSpray source at a flow rate of 5 μ L.min⁻¹ with a capillary voltage of 4.5kV to enhance the production of radical cation species, a source temperature of 100°C and a desolvation temperature of 200°C. Ion mobility was performed using N₂ as drift gas and a wave height of 40V. Wave velocities and drift gas flow were varied to ensure the robustness of the method. Wave velocities varied between 400 and 800 m.s⁻¹ and drift gas flow varied between 50 and 110 mL.min⁻¹.

Data treatment

Drift times and arrival time distributions (ATDs) were extracted using Waters MassLynx. Drift times and ATDs were converted into collisional cross section (CCS) values in helium by means of the polymer calibration described in Ref [5] using commercial PEG samples with average molecular weights of 600, 1000 and 2000. The experiments were performed three times and the presented CCS are mean values, whereas the percentages in brackets are the standard deviations.

The arrival time distribution of the mixture of **4a** and **4b** was deconvoluted into two symmetric gaussians using the Multiple Peak Fit function available in Origin 9.0. The fit between the sum of the two deconvoluted curves and the experimental data was characterized by a $R^2 > 0.998$.

Computational chemistry

Each structure considered in the present paper was built with GaussView 5.0.9 and the geometries were optimized at the quantum-chemical level with the Gaussian 09 A02 package[6], using the ω B97X-D functional and a 6-31G(d,p) basis set. [7]

Theoretical CCS were calculated using Collidoscope[8] via the trajectory method, using 6 energy states and He as drift gas. The van der Waals parameters for the F atom, not available in Collidoscope, were implemented from values available in Mobcal.[9]

References:

1. Thirion, D., Poriel, C., Rault-Berthelot, J., Barrière, F., Jeannin, O.: (2,1-a)-Indenofluorene Derivatives: Syntheses, X-ray Structures, Optical and Electrochemical Properties. *Chem. - A Eur. J.* 16, 13646–13658 (2010). doi:10.1002/chem.201001830
2. Poriel, C., Rault-Berthelot, J., Barrière, F., Slawin, A.M.Z.: New Dispiro Compounds : Synthesis and Properties. *Org. Lett.* 10, 4435–4438 (2008)
3. Poriel, C., Barrière, F., Thirion, D., Rault-Berthelot, J.: Encumbered DiSpiro [Fluorene – IndenoFluorene]: Mechanistic Insights. *Chem. - A Eur. J.* 15, 13304–13307 (2009). doi:10.1002/chem.200902006
4. Romain, M., Tondelier, D., Geffroy, B., Jeannin, O., Jacques, E., Rault-Berthelot, J., Poriel, C.: Donor/Acceptor Dihydroindeno[1,2-a]fluorene and Dihydroindeno[2,1-b]fluorene: Towards New Families of Organic Semiconductors. *Chem. - A Eur. J.* 21, 9426–9439 (2015). doi:10.1002/chem.201500336
5. Duez, Q., Chirot, F., Liénard, R., Josse, T., Choi, C., Coulembier, O., Dugourd, P., Cornil, J., Gerbaux, P., De Winter, J.: Polymers for Traveling Wave Ion Mobility Spectrometry Calibration. *J. Am. Soc. Mass Spectrom.* 28, 2483–2491 (2017). doi:10.1007/s13361-017-1762-4
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Had, D.J.F.: *Gaussian 09*, (2009)
7. Chai, J.-D., Head-Gordon, M.: Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* 10, 6615–6620 (2008). doi:10.1039/b810189b
8. Ewing, S.A., Donor, M.T., Wilson, J.W., Prell, J.S.: *Collidoscope: An Improved Tool for*

Computing Collisional Cross-Sections with the Trajectory Method. *J. Am. Soc. Mass Spectrom.* 28, 587–596 (2017). doi:10.1007/s13361-017-1594-2

9. Mesleh, M.F., Hunter, J.M., Shvartsburg, A.A., Schatz, G.C., Jarrold, M.F.: Structural Information from Ion Mobility Measurements: Effects of the Long-Range Potential. *J. Phys. Chem.* 100, 16082–16086 (1996). doi:10.1021/jp961623v