The fluorine atom as a halogen bond donor, *viz.* a positive site

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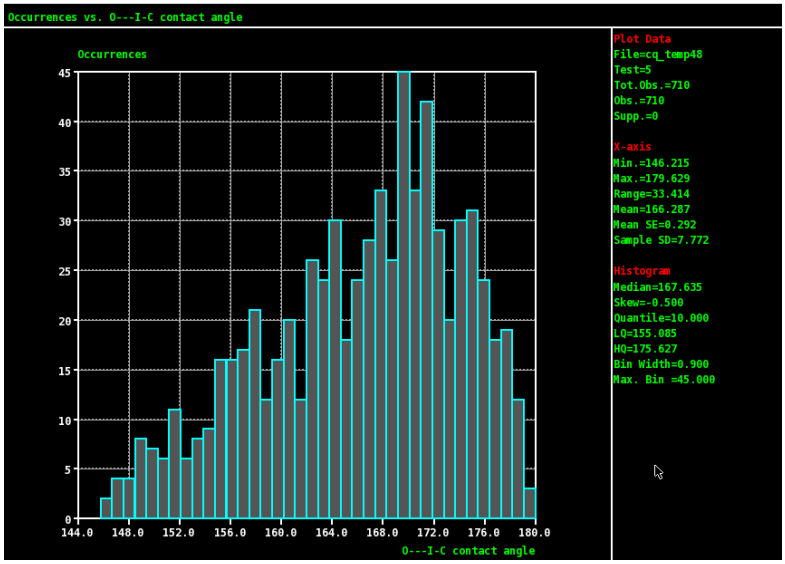
S1. Analyses of the Cambridge Structure Database (CSD).

Data from CSD version 5.32 (November 2010 + 1 update), ConQuest 1.13.

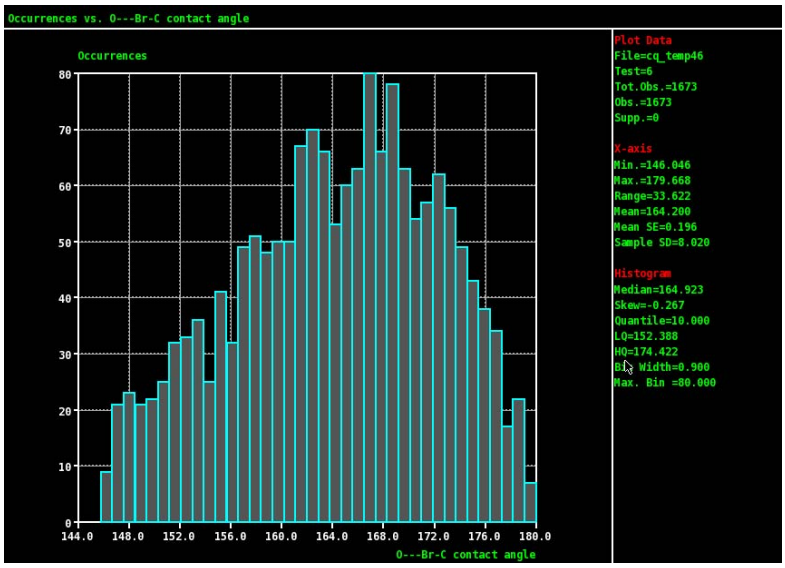
S1.1. Histogram of occurrences as a function of the O···I-C contact angle.

Monovalent iodine with no charge; structures (589 hits) with $R_{factor} \leq 0.05$, not disordered, no powder, no errors.



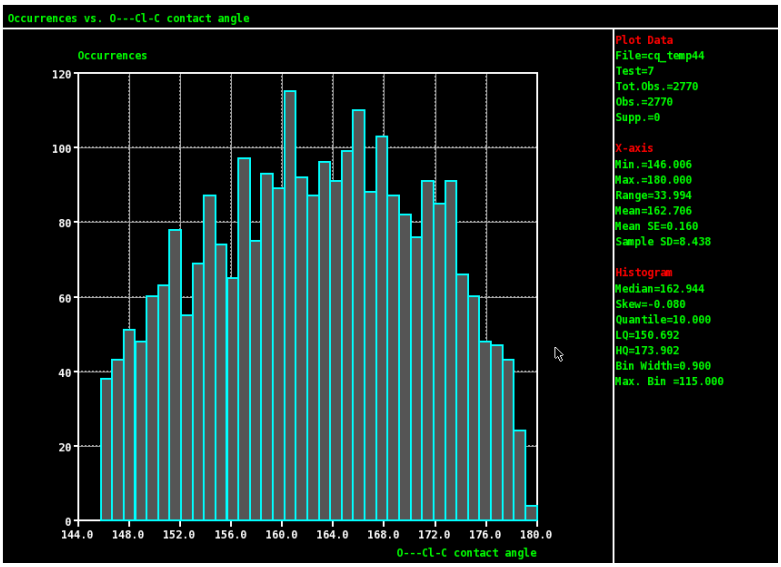
S1.2. Histogram of occurrences as a function of the O···Br-C contact angle.

Monovalent bromine with no charge; structures (1421 hits) with $R_{factor} \leq 0.05$, not disordered, no powder, no errors.



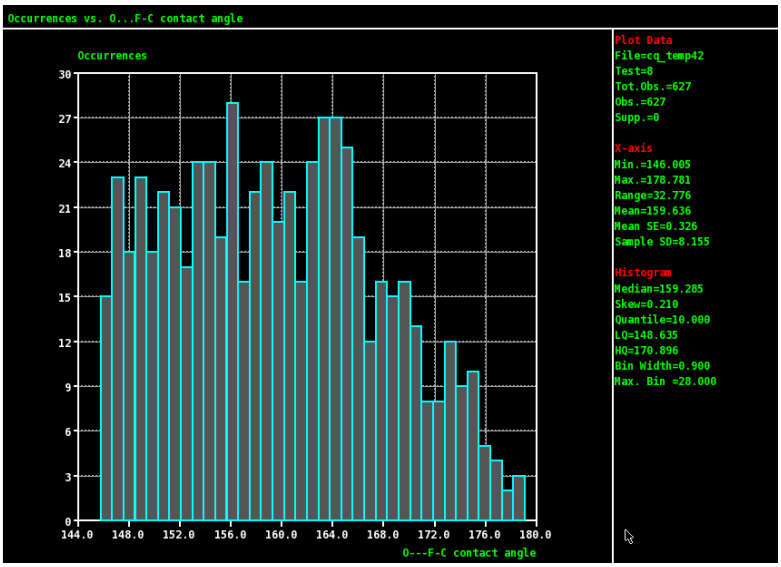
S1.3. Histogram of occurrences as a function of the O···Cl-C contact angle.

Monovalent chlorine with no charge; structures (2355 hits) with $R_{factor} \leq 0.05$, not disordered, no powder, no errors.



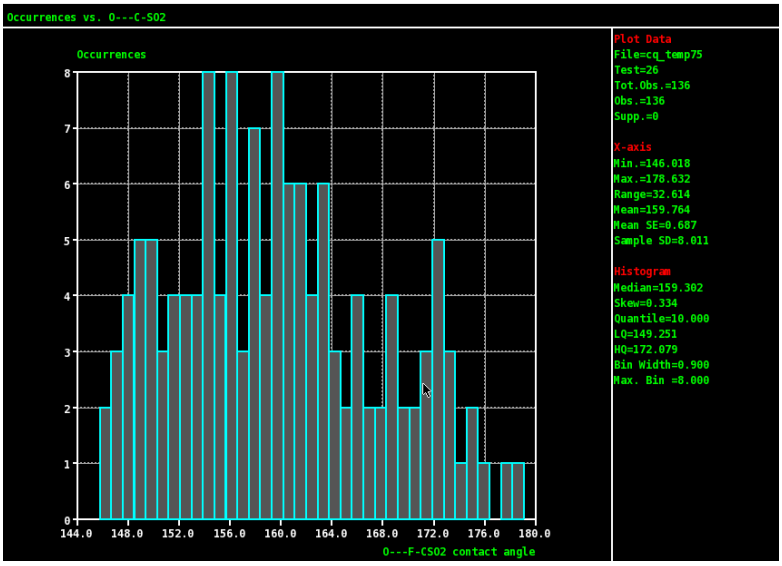
S1.4. Histogram of occurrences as a function of the O···F-C contact angle.

Monovalent fluorine with no charge; structures (556 hits) with $R_{factor} \leq 0.05$, not disordered, no powder, no errors.



S1.5. Histogram of occurrences as a function of the O···F-C-SO_2 contact angle.

Monovalent fluorine with no charge; structures (124 hits) with $R_{factor} \leq 0.1$, not disordered, no powder, no errors.



S2. Calculation of the electrostatic potential.

In this work, we have optimized molecular geometries and have calculated the electrostatic potential V(**r**) with the B3PW91/6-31G(d,p) procedure. This has been used in previous studies, and therefore allows comparisons of the fluorine surface electrostatic potentials V_S(**r**) to those of other halogens. The Gaussian 09 code [1] was utilized for geometry optimizations and for obtaining wave functions, and the Wave Function Analysis – Surface Analysis Suite [2] for V_S(**r**).

[1] Gaussian 09, Revision **A.1**, 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. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S3. Representation of selected structures from the CSD that meet the standard geometric requirements for fluorine functioning as an XB donor.

The digits close to the XB (dashed lines) are the covalent bond/XB angle around fluorine and the normalized contact (Nc), namely the ratio Nc = Dij/(rvdWi + rvdWj), where Dij is the distance between the atoms i and j and rvdWi and rvdWj are the van der Waals radii for fluorine and oxygen, 147 and 152 pm, respectively.

S3.1. Ball and stick representation of bis(1-(Difluoro-oxo-λ^6-sulfanylidene)-2-fluoro-2-oxoethyl)-mercury (CSD code VIHNEF) [2]

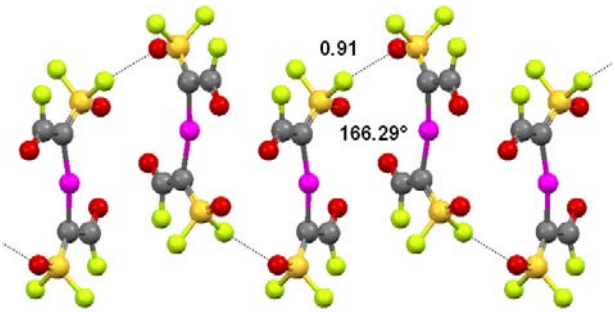


Fig. S3.1. Ball and stick representations of 1D infinite (view along *a*) chains formed by bis(1-(Difluoro-oxo-λ^6-sulfanylidene)-2-fluoro-2-oxoethyl)-mercury. Colour code: grey, carbon; yellow, sulfur; red, oxygen; light green, fluorine; purple, mercury.

[2] J. Bittner and K. Seppelt *Chem.Ber.*, 1991, **124**, 87.

S3.2. Ball and stick representation of mer-tris(Fluorosulfato)-tricarbonyl-iridium(III) (CSD code ZUBNIT) [3]

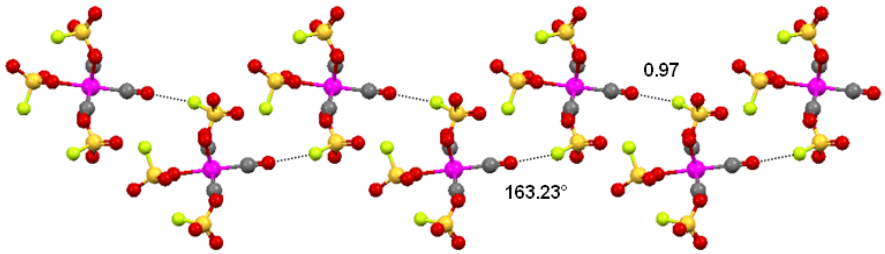


Fig. S3.2. Ball and stick representations of 1D infinite chains formed by mer-tris(Fluorosulfato)-tricarbonyl-iridium(III). Colour code: grey, carbon; yellow, sulfur; red, oxygen; light green, fluorine; purple, iridium.

S3.3. Ball and stick representation of 1,1,3,3-tetrakis(Trifluoromethanesulfonyl)propane (CSD code SIZPIB) [4]

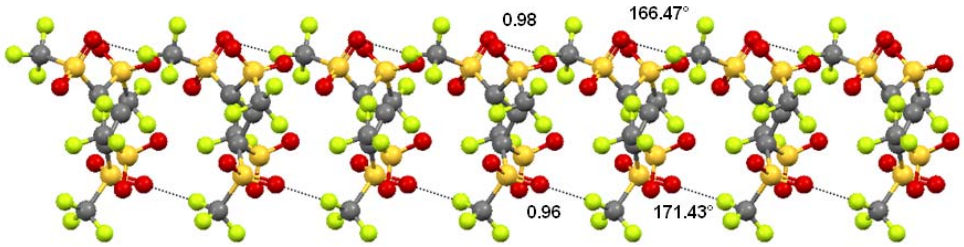


Fig. S3.3. Ball and stick representations of supramolecular ribbon (view along *b*) formed by 1,3,3-tetrakis(Trifluoromethanesulfonyl)propane. Colour code: grey, carbon; yellow, sulfur; red, oxygen.

[3] C. Wang, A. R. Lewis, R. J. Batchelor, F. W. B. Einstein, H. Willner and F.Aubke *Inorg.Chem.* 1996, **35**, 1279.
[4] A. Takahashi, H. Yanai and T. Taguchi *Chem.Commun*., 2008, 2385.

S3.4. Ball and stick representation of N-Methyl-N-nitro-4-(trifluoromethyl)perfluorophenylamine (CSD code XIHLUV) [5]

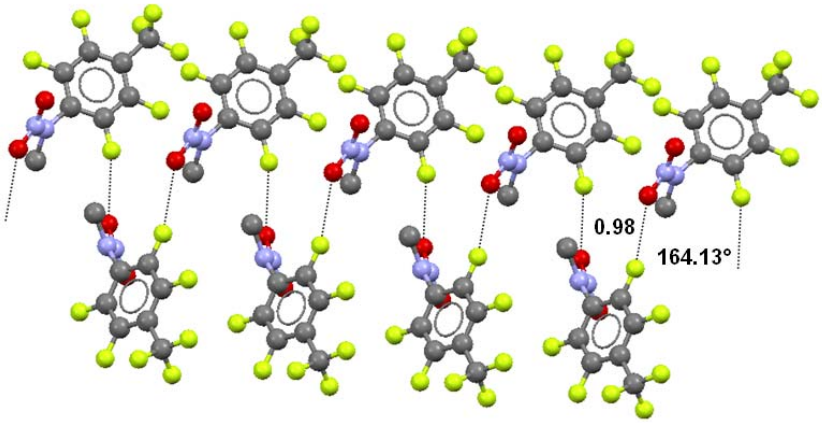


Fig. S3.4. Ball and stick representations of supramolecular ribbon (view along *c*) formed by N-Methyl-N-nitro-4-(trifluoromethyl)perfluorophenylamine. Colour code: grey, carbon; yellow, sulfur; red, oxygen; blue, nitrogen. Hydrogen atoms are omitted for clarity.

S3.5. Ball and stick representation of 1-Ethyl-3-methyl-4-nitroimidazolium trifluoromethanesulfonate (CSD code GEDLEH) [6]

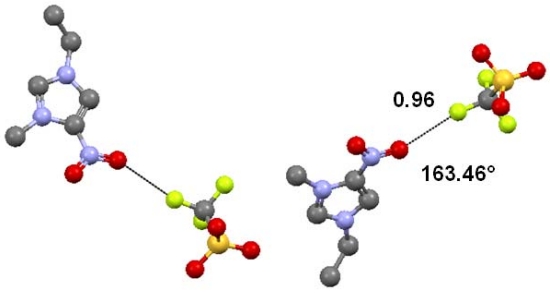


Fig. S3.5. Ball and stick representations of dimeric system formed by 1-ethyl-3-methyl-4-nitroimidazolium trifluoromethanesulfonate. Colour code: grey, carbon; yellow, sulfur; red, oxygen; blue, nitrogen. Hydrogen atoms are omitted for clarity.

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[5] V. E. Platonov, A. Haas, M. Schelvis, M. Lieb, K. V. Dvornikova, O. I. Osina and Y. V. Gatilov *J.Fluorine Chem*., 2001, **109**, 131.
[6] A. R. Katritzky, H. Yang, D. Zhang, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert and R. D. Rogers *New J.Chem*., **2006**, *30*, 349.

S3.6. Ball and stick representation of (η^5-pentamethylcyclopentadienyl)-(ethane-1,2-diol-O,O')-(nitrosyl)-ruthenium(II) bis(trifluoromethanesulfonate) (CSD code HIVDIA) [7]

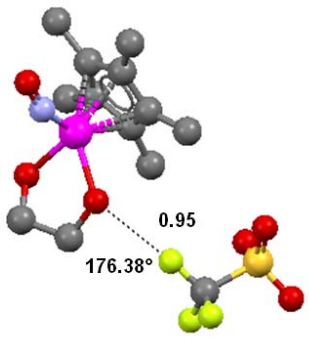

Fig. S3.5. Ball and stick representations of discrete supramolecular system formed by η^5-pentamethylcyclopentadienyl)-(ethane-1,2-diol-O,O')-(nitrosyl)-ruthenium(II) bis(trifluoromethanesulfonate). Colour code: grey, carbon; yellow, sulfur; red, oxygen; blue, nitrogen; purple, ruthenium. Hydrogen atoms are omitted for clarity.

[7] S. Munie, A. Larsen and M. Gembicky *Acta Crystallogr.,Sect.E:Struct.Rep.Online* 2008, **64**, m293.