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

Pierangelo Metrangolo,*[a,b] Jane S. Murray,[c] Tullio Pilati,[a,d] Peter Politzer,[c] Giuseppe Resnati*[a,b,d] and Giancarlo Terraneo[a,b]

[a] NFMLab, Dept. Chemistry, Materials and Chemical Engineering. ''Giulio Natta'',
Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy; Fax: +39.02.2399.3180;
Tel: +39.02.2399.3041 (P. M.), .3032 (G. R.);
E-mail: pierangelo.metrangolo@polimi.it , giuseppe.resnati@polimi.it.
[b] CNST-IIT@POLIMI, Via Pascoli 70/3, 20133 Milan, Italy.
[c] CleveTheoComp, 1951 W. 26th Street, Suite 409. Cleveland, OH 44113, USA.
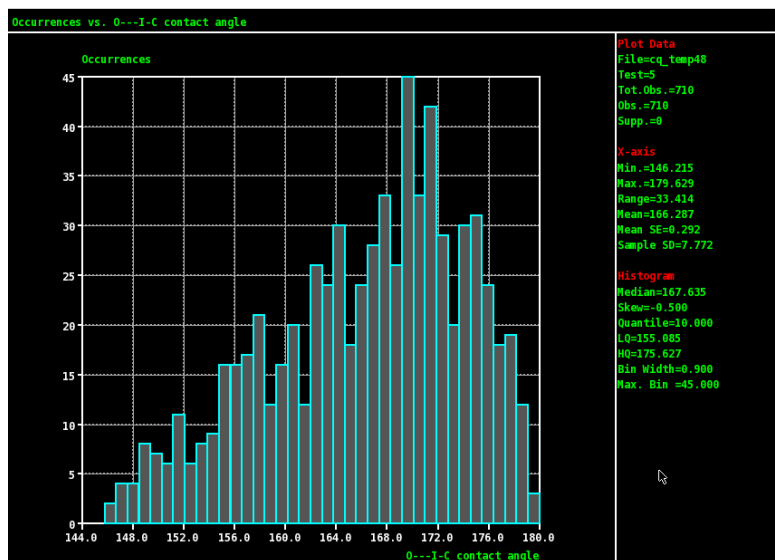*[d] ISTM-CNR, Università di Milano, Via Venezian 21, 20133 Milan, Italy.*

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

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

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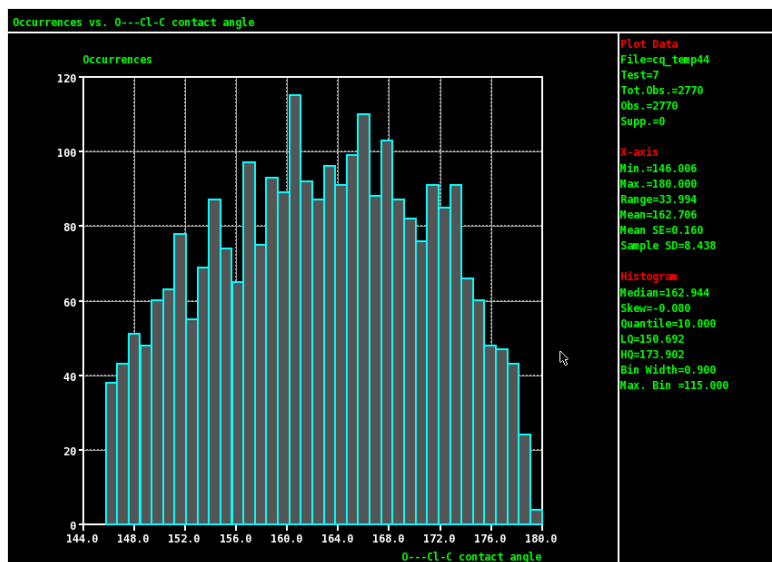
S1.2. Histogram of occurrences as a function of the O···Br-C contact angle.

Monovalent bromine with no charge; structures (1421 hits) with $R_{factor} \leq$ 0.05, not disordered, no powder, no errors.
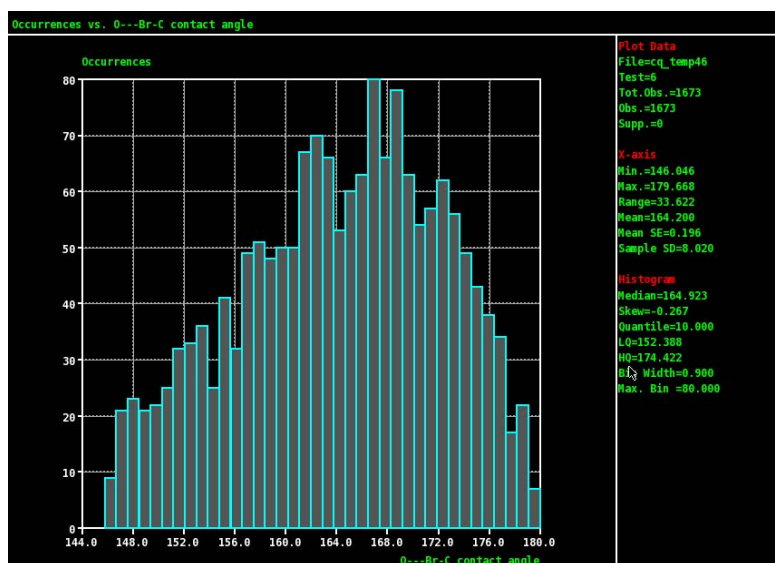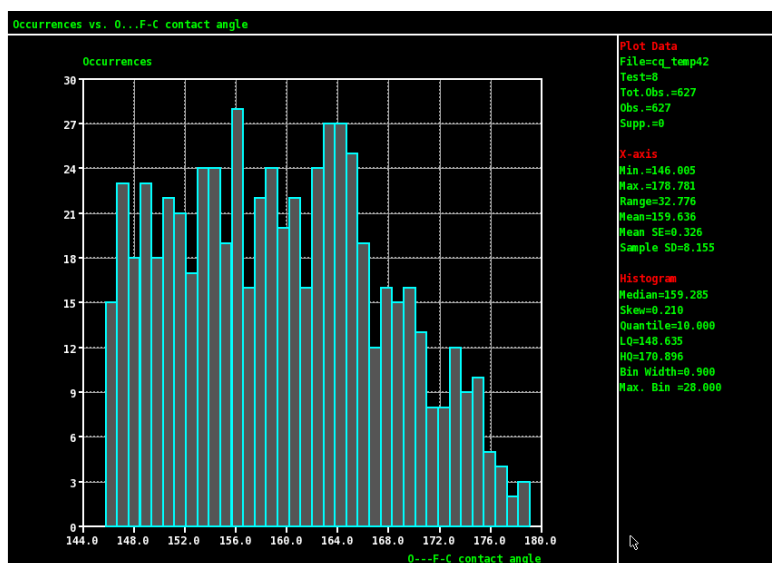
S1.3. Histogram of occurrences as a function of the O···Cl-C contact angle.

Monovalent chlorine with no charge; structures (2355 hits) with $R_{factor} \leq$ 0.05, not disordered, no powder, no errors.
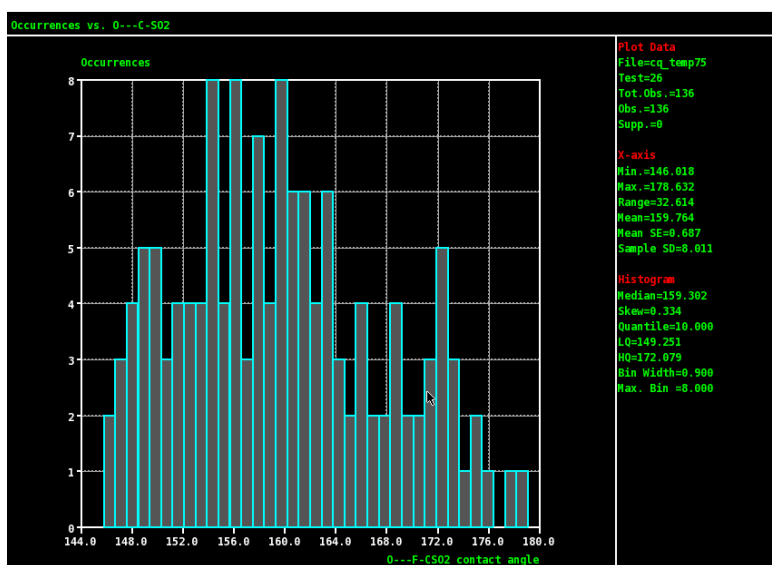
S1.4. Histogram of occurrences as a function of the O···F-C contact angle.

Monovalent fluorine with no charge; structures (556 hits) with $R_{factor} \leq 0.05$, ₅ 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 $V(\mathbf{r})$ 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 $V_S(\mathbf{r})$ 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 $V_S(\mathbf{r})$.

[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.

5 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.

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S3.1. Ball and stick representation of bis(1-(Difluoro-oxo-λ^6-sulfanylidene)-2-fluoro-2-oxoethyl)-mercury (CSD code VIHNEF) [2]
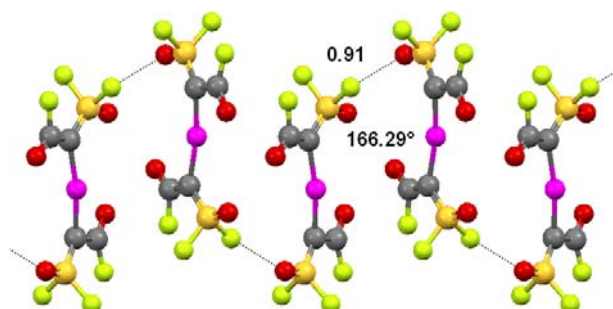
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Fig. S3.1. Ball and stick representations of 1D infinite (view along *a*) chains formed by bis(1-(Difluoro-oxo-λ^6-sulfanylidene)-2-fluoro-2-oxoethyl)-mercury. Colour code: grey, carbon; yellow, sulfur; red, oxygen; light green, fluorine; purple, mercury.
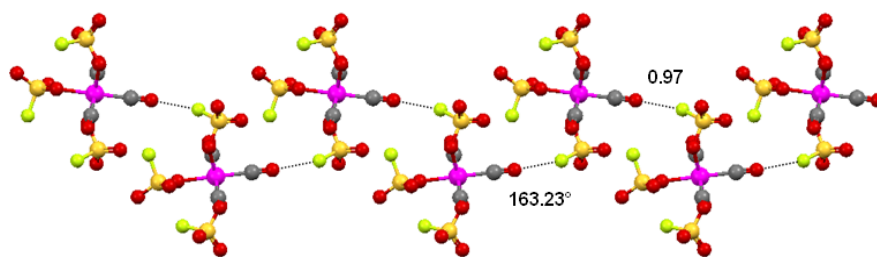
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[2] J. Bittner and K. Seppelt *Chem.Ber.,* 1991, **124**, 87.

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

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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.

10 S3.3. Ball and stick representation of 1,1,3,3-tetrakis(Trifluoromethanesulfonyl)propane (CSD code SIZPIB) [4]
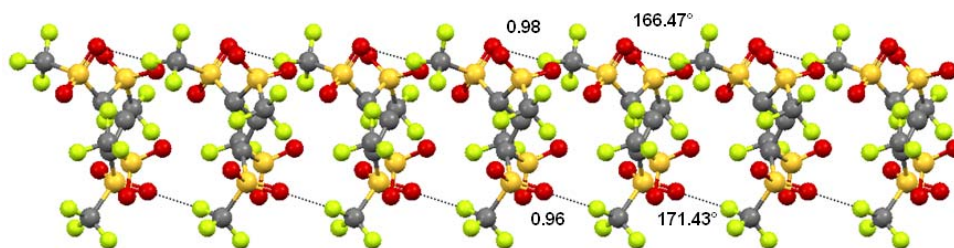
Fig. S3.3. Ball and stick representations of supramolecular ribbon (view along *b*) formed by
15 1,3,3-tetrakis(Trifluoromethanesulfonyl)propane. Colour code: grey, carbon; yellow, sulfur; red, oxygen.

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[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]
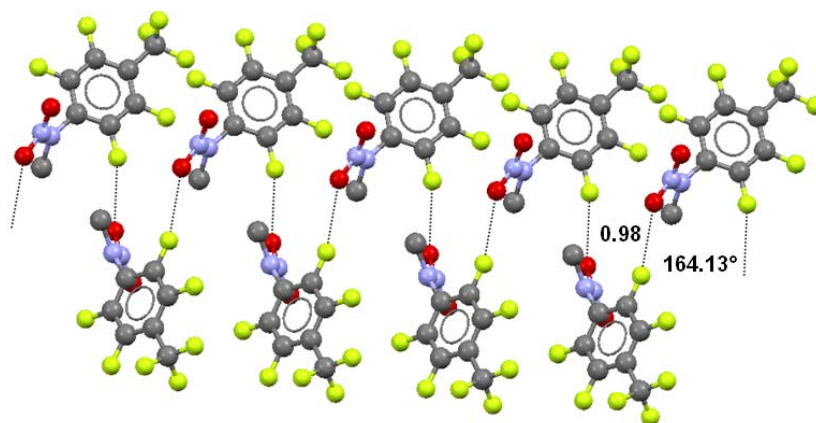

Fig. S3.4. Ball and stick representations of supramolecular ribbon (view along *c*) formed by N-Methyl-N-nitro-4-(trifluoromethyl)perfluorophenylamine. Colour code: grey, carbon; yellow, sulfur; red, oxygen; blue, nitrogen. Hydrogen atoms are omitted for clarity.

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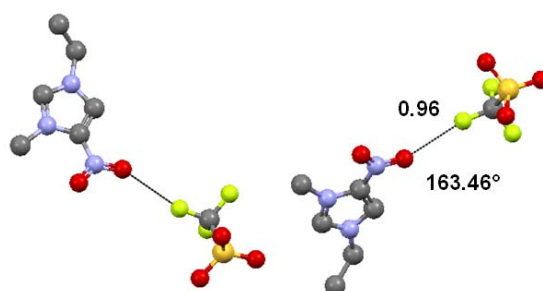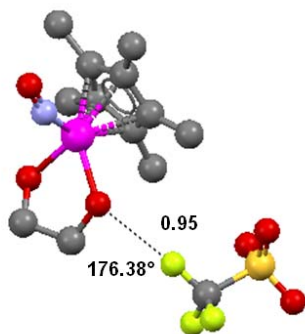

Fig. S3.5. Ball and stick representations of dimeric system formed by 1-ethyl-3-methyl-4-nitroimidazolium trifluoromethanesulfonate. Colour code: grey, carbon; yellow, sulfur; red, oxygen; blue, nitrogen. Hydrogen atoms are omitted for clarity.

[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.