

Supplementary Information  
for

**Non-covalent interactions in organic radicals: pancake-,  $\sigma$ -hole-, and H-bonding  
in F<sub>2</sub>HbimDTDA**

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## EXPERIMENTAL SECTION

### Synthesis of Organic Starting Materials.

**5,6-Difluoro-2-(trichloromethyl)benzimidazole.** 4,5-Difluoro-1,2-diaminobenzene (5.0112 g, 35 mmol) was dissolved in glacial acetic acid (150 mL), forming a deep brown solution. Methyl 2,2,2-trichloroacetimidate (4.5 mL, 36 mmol) was added and the solution was stirred for two hours. Deionized water (400 mL) was added, resulting in an immediate terracotta-colored precipitate. The solid was collected by vacuum filtration and washed with water (1000 mL) until the filtrate was colorless. The solid was thoroughly dried to yield the brown-red product; crude yield 8.2381g (87%). ATR-IR (neat, cm<sup>-1</sup>): 2988m, 2929m, 2847m, 2102, w, 1736w, 1637w, 1608m, 1524w, 1488s, 1468s, 1428s, 1369w, 1346w, 1318w, 1255m, 1199m, 1157m, 1135m, 1037m, 1019w, 905s, 860s, 834s, 778m, 746w, 682m, 639m, 505m, 477w, 438w. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO): 8.40 (1H, s), 7.73 (2H, m) ppm. <sup>13</sup>C NMR (101 MHz, d<sub>6</sub>-DMSO): 152.3, 88.2 ppm.

**5,6-Difluorobenzimidazole-2-carbonitrile.** 5,6-Difluoro-2-(trichloromethyl)benzimidazole (7.6891 g, 28 mmol) was added portion-wise to freshly condensed liquid ammonia (200 mL) in a 3-necked round bottom flask equipped with a dry ice condenser and argon inlet. The resulting dark brown mixture was allowed to stir while slowly warming overnight. After the ammonia had completely boiled off, the brown solid was stirred in pH 5 water (300 mL) for 2 hours. The dark brown solid was collected by vacuum filtration and stirred in pH 7 water (500 mL) for 15 minutes before the solid was collected again and then stirred into aqueous sodium carbonate. This mixture was washed with ether (200 mL), and the organic layer was discarded. The aqueous layer was acidified to pH 5 and the resulting light brown powder was collected via vacuum filtration and thoroughly dried; Yield 2.5490 g (50%). ATR-IR (neat, cm<sup>-1</sup>): 3133w, 3080w, 3067w, 2970m, 2905m, 2816m, 2755m, 2672m, 2628m, 2244s, 1720w, 1640w, 1602m, 1526w, 1516w, 1489s, 1455s, 1443m, 1423s, 1379w, 1367m, 1345m, 1261s, 1202m, 1171w, 1159s, 1139m, 1112w, 1025m, 887m, 866s, 857s, 755m, 689m, 645m, 617w, 564w, 479w, 438w, 427w. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO): 7.87 (dd, 2H, J = 16 Hz, 2.4 Hz) ppm. <sup>13</sup>C NMR (101 MHz, d<sub>6</sub>-DMSO): 150.1, 147.7, 125.9, 112.0 ppm.

### CRYSTALLOGRAPHIC DETAILS

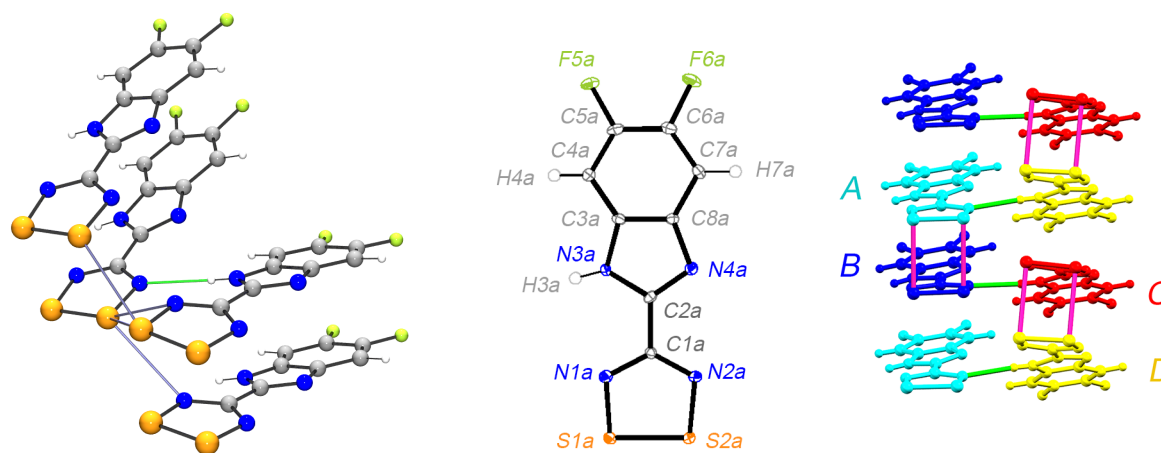
*Powder X-Ray Diffraction (PXRD).* Data were collected at Guelph using a PANalytical Empyrean diffractometer in a reflection (Bragg-Brentano) geometry with Cu K $\alpha$  radiation source, Ni K $\beta$  filter and PIXcel<sup>1D</sup> linear detector. Two samples of F<sub>2</sub>HbimDTDA were prepared, one of material sublimed at 145 °C and the other of material sublimed at 180 °C. The samples were loaded into a 1 mm diameter capillary (borosilicate glass, 10  $\mu$ m wall, purchased from Charles Supper) under argon gas and flame sealed. The sealed capillary was mounted on a goniometer head equipped with a brass holder and secured with modelling clay. The sample was then mounted onto a spinning capillary stage and adjusted so that 1 cm of the capillary length was within the window of detection. Powder diffractograms were recorded in the 3.5 - 40° 2 $\theta$  range while spinning the sample. Data collection was controlled with X'Pert Data Collector Software.<sup>1</sup>

*Data Collection and Processing of the Data Collected at 110 K.* The crystals were grown by sublimation. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9867 reflections with  $6.14^\circ < 2\theta < 66.66^\circ$ . The data collection strategy was a number of  $\omega$  and  $\varphi$  scans which collected data up to  $72.756^\circ$  ( $2\theta$ ). The frame integration was performed using SAINT.<sup>2</sup> The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.<sup>3</sup>

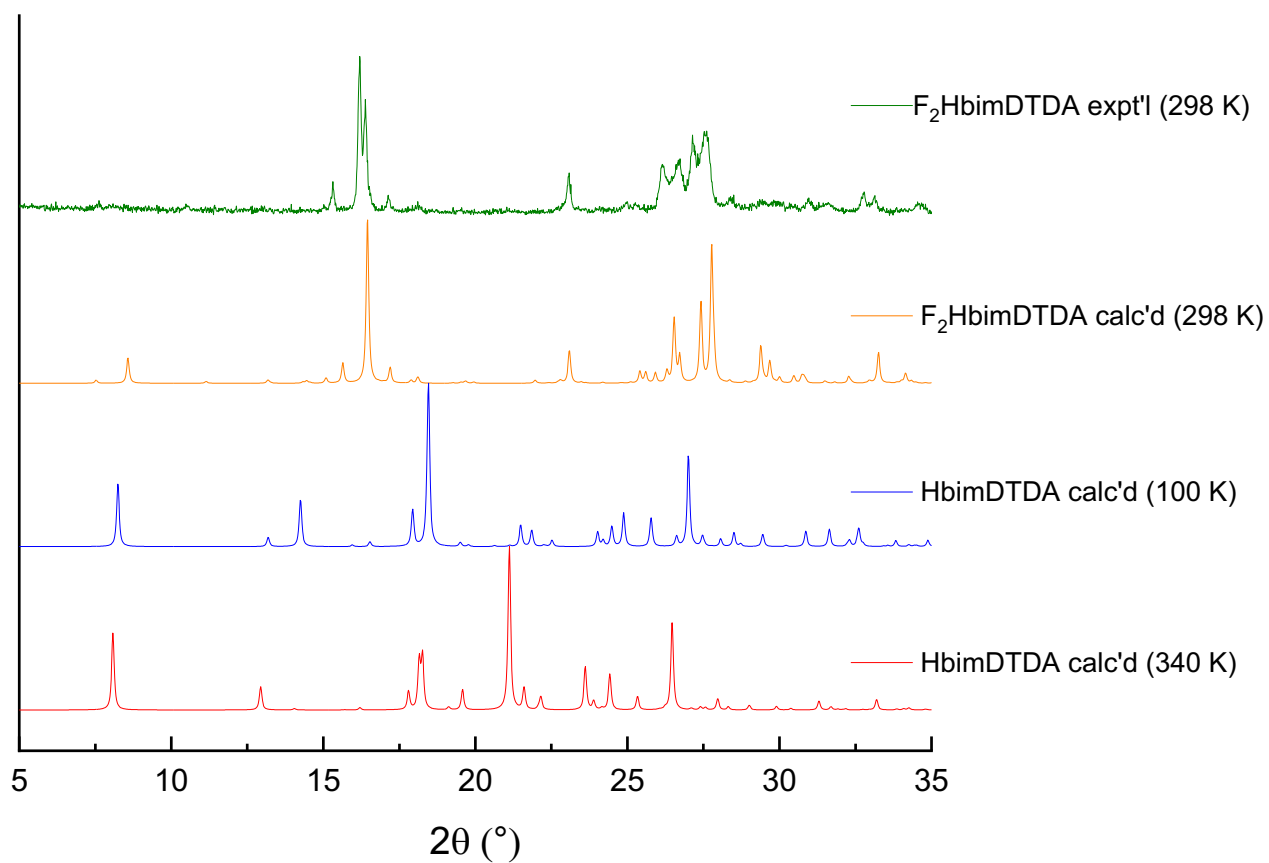
*Structure Solution and Refinement of the Data Collected at 110 K.* The structure was solved by using a dual space methodology using the SHELXT program.<sup>4</sup> All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. There were 4 symmetry independent molecules in the asymmetric unit. The atom names had an A, B, C, or D appended to the naming and numbering scheme to differentiate the symmetry independent molecules. The structural model was fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELX suite of crystallographic software. **Error! Bookmark not defined.** Graphic plots were produced using the Mercury program suite.<sup>5</sup> Additional information and other relevant literature references can be found in the reference section of this website (<http://xray.chem.uwo.ca>).

*Data Collection and Processing of the Data Collected at 120, 298, and 350 K.* The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker APEX-II Quasar diffractometer at a temperature of 120(2) K. The unit cell dimensions were determined from a symmetry constrained fit of: 4340 reflections with  $6.68^\circ < 2\theta < 50.0^\circ$  at 120 K; 1388 reflections with  $6.66^\circ < 2\theta < 46.34^\circ$  at 298 K; 1544 reflections with  $6.64^\circ < 2\theta < 40.66^\circ$  at 350 K. The data collection strategy was a number of  $\omega$  and  $\varphi$  scans which collected data up to:  $50.266^\circ$  ( $2\theta$ ) at 120 K;  $46.634^\circ$  ( $2\theta$ ) at 298 K;  $41.746^\circ$  ( $2\theta$ ) at 35 K. The frame integration was performed using SAINT.<sup>2</sup> The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.<sup>3</sup>

*Structure Solution and Refinement of the Data Collected at 120, 298, and 350 K.* The structure was solved by using a dual space methodology using the SHELXT 2014/4 (Sheldrick, 2014) program.<sup>6</sup> All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2016/6 (Sheldrick, 2016) program from the SHELX suite of crystallographic software. **Error! Bookmark not defined.**



**Figure S1.** Excerpts from the 110 K crystal structure of F<sub>2</sub>HbimDTDA illustrating (left) the network of intermolecular contacts (slate blue) that support the hydrogen bonding interactions (green); (center) the atom labels; (right) the molecule labels



**Figure S2.** Powder X-Ray diffraction patterns of a bulk sample of  $F_2HbimDTDA$  (green), with calculated patterns of  $F_2HbimDTDA$  (orange) and both phases of HbimDTDA (blue and red). Calculated patterns are from the crystal structures at temperatures as indicated. Clearly, more than one phase of  $F_2HbimDTDA$  is present in the bulk sample, but there is no indication that either of the phases observed for HbimDTDA is present.

**Table S1.** Summary of Crystallographic Data for F<sub>2</sub>HbimDTDA

|  |  |                       |             |             |
|--|--|-----------------------|-------------|-------------|
| Formula  | C <sub>8</sub> H <sub>3</sub> F <sub>2</sub> N <sub>4</sub> S <sub>2</sub> |                       |             |             |
| Formula Weight (g/mol)                             | 257.26   |                       |             |             |
| Crystal Dimensions (mm)                            | 0.322 × 0.112 × 0.036  | 0.210 × 0.030 × 0.010 |             |             |
| Crystal Color and Habit                            | red plate  | orange needle         |             |             |
| Crystal System                                     | monoclinic   | monoclinic            |             |             |
| Space Group  | Cc   | Cc                    |             |             |
| Temperature, K                                     | 110(2)   | 120(2)                | 298(2)      | 350(2)      |
| a, Å   | 6.9858(17)   | 6.9799(8)             | 7.0744(7)   | 7.1142(17)  |
| b, Å   | 23.433(6)  | 23.445(2)             | 23.4691(18) | 23.512(5)   |
| c, Å   | 21.589(5)  | 21.580(2)             | 21.7493(16) | 21.797(4)   |
| β, °   | 97.399(8)  | 97.545(5)             | 98.044(4)   | 98.388(10)  |
| V, Å <sup>3</sup>                                  | 3504.5(15)   | 3500.7(6)             | 3575.5(5)   | 3607.4(13)  |
| Number of reflections to determine final unit cell | 9867   | 4340                  | 1388        | 1544        |
| Min and Max 2θ for cell determination, °           | 6.14, 66.66  | 6.68, 50.0            | 6.66, 46.34 | 6.64, 40.66 |
| Z  | 16   |                       |             |             |
| F(000)   | 2064   |                       |             |             |
| ρ (g/cm <sup>3</sup> )                             | 1.950  | 1.953                 | 1.912       | 1.895       |
| λ, Å, (MoKα)                                       | 0.71073  |                       |             |             |
| μ, (cm <sup>-1</sup> )                             | 0.611  | 0.612                 | 0.599       | 0.594       |
| Diffractometer Type                                | Bruker Kappa Axis Apex2  | Bruker APEX-II Quasar |             |             |
| Scan Type(s)                                       | phi and omega scans  | phi and omega scans   |             |             |
| Max 2θ for data collection, °                      | 72.756   | 50.266                | 46.634      | 41.746      |
| Measured fraction of data                          | 0.999  | 0.993                 | 0.998       | 0.998       |
| Number of reflections measured                     | 76812  | 27173                 | 16119       | 18048       |
| Unique reflections measured                        | 13783  | 5700                  | 4741        | 3638        |
| R <sub>merge</sub>                                 | 0.0481   | 0.0637                | 0.1134      | 0.1112      |
| Number of reflections included in refinement       | 13783  | 5700                  | 4741        | 3638        |
| Cut off Threshold Expression                       | I > 2σ(I)  |                       |             |             |

| Structure refined using                                    | full matrix least-squares using F <sup>2</sup>                    |  |   |  |
|--|---|--|---|--|
| Weighting Scheme   | $w=1/[\sigma^2(F_o^2)+(0.0514P)^2]$<br>where $P=(F_o^2+2F_c^2)/3$ | $w=1/[\sigma^2(F_o^2)+(0.0386P)^2+1.2672P]$ where $P=(F_o^2+2F_c^2)/3$ | $w=1/[\sigma^2(F_o^2)+(0.0145P)^2]$<br>where $P=(F_o^2+2F_c^2)/3$ | $w=1/[\sigma^2(F_o^2)+(0.0140P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Number of parameters in least-squares                      | 625   | 577  |   |  |
| R <sub>1</sub>   | 0.0445  | 0.0383   | 0.0494  | 0.0376   |
| wR <sub>2</sub>  | 0.0872  | 0.0766   | 0.0807  | 0.0621   |
| R <sub>1</sub> (all data)                                  | 0.0625  | 0.0523   | 0.1021  | 0.0716   |
| wR <sub>2</sub> (all data)                                 | 0.0943  | 0.0808   | 0.0938  | 0.0700   |
| GOF  | 0.997   | 1.039  | 0.983   | 0.965  |
| Maximum shift/error  | 0.001   | 0.000  | 0.000   | 0.000  |
| Min & Max peak heights on final ΔF Map (e <sup>-</sup> /Å) | -0.493, 0.656   | -0.337, 0.353  | -0.287, 0.278   | -0.213, 0.208  |
| CCDC   | 2072282   | 2072283  | 2072284   | 2072285  |

Where:  $R_1 = \sum (|F_o| - |F_c|) / \sum F_o$ ;  $wR_2 = [ \sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4 ]^{1/2}$ ;

GOF =  $[ \sum w (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.}) ]$

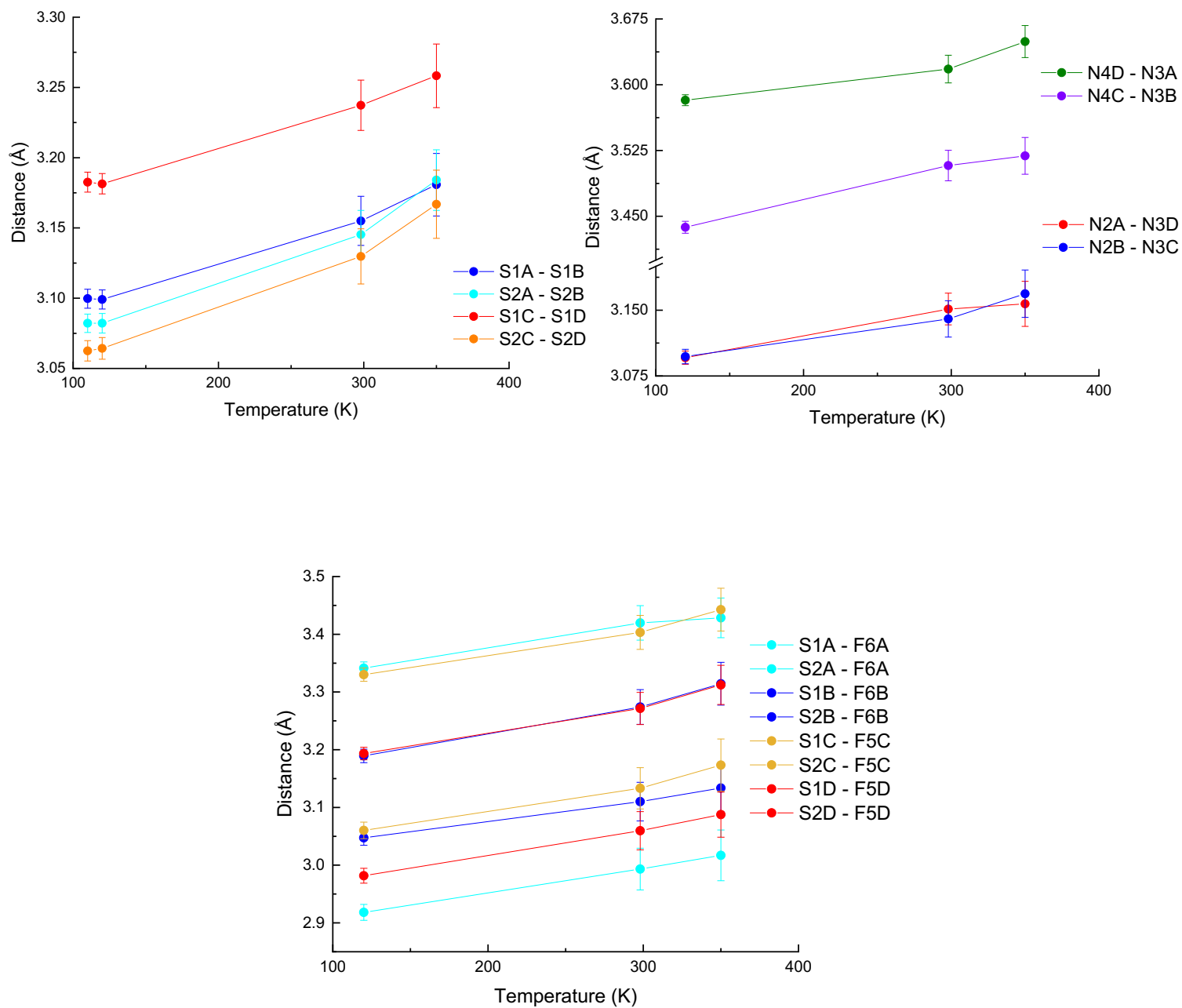
**Table S2.** Select characteristic DTDA measures of the intra- and inter-molecular distances from the crystal structure of F<sub>2</sub>HbimDTDA at 110 K. Molecules A – D are defined according to the labelling scheme in the CIF (see Fig. S1). Distances are reported in Å and angles in °.

| Molecule A   | Molecule B            | Molecule C | Molecule D            |
|--|-----------------------|------------|-----------------------|
| Observed S – S bond distance within each thiazyl ring (S1 – S2)                            |                       |            |                       |
| 2.091(1)   | 2.079(1)              | 2.089(1)   | 2.096(1)              |
| Calculated libration-corrected S – S bond distance within each thiazyl ring (S1 – S2)      |                       |            |                       |
| 2.0939   | 2.0815                | 2.0921     | 2.0990                |
| Intermolecular S – S distance within a pancake bond  |                       |            |                       |
| S1A – S1B    3.093(1)  | S1C – S1D    3.176(1) |            | S2C – S2D    3.055(1) |
| S2A – S2B    3.076(1)  |                       |            |                       |
| Dihedral angle between planes defined by the atoms of the benzimidazole and the DTDA rings |                       |            |                       |
| 6.96   | 9.73                  | 15.03      | 11.51                 |

*Intramolecular and Intermolecular Distance Corrections.* Due to the multi-temperature nature of this study, it was important to account for systematic errors in the calculated distances due to libration and other molecular motions in the crystal. The rigid body motion tensors,<sup>7</sup> **T**, **L**, and **S**, were calculated for each molecule in the asymmetric unit using PLATON<sup>8</sup> and a libration correction was applied to the intramolecular distances. The intermolecular contacts were corrected by the method of Busing and Levy<sup>9</sup> to give upper and lower limits to the contact distances as well as a distance assuming uncorrelated motion of the two atoms of interest. The corrections to the intermolecular contacts were performed using the DISTCOR program.<sup>10</sup> The corrected distances are tabulated in Table S3 and plotted in Figure S3. It is worth noting that the changes in distances as a function of temperature observed in the distance correction models follow the trend established by the uncorrected distances.

**Table S3.** Uncorrected values for select contact distances (Å) and angles (°) in F<sub>2</sub>HbimDTDA at variable temperatures as output by the Mercury software;<sup>5</sup> Corrected contact distances (Å) in F<sub>2</sub>HbimDTDA at variable temperatures as output by the DISTCOR program using three models for the correlation of motion between atoms;<sup>10</sup> labelling convention shown in Figure S1

|  | 120 K               |              |              |                    | 298 K                |              |              |                    | 350 K                |              |              |                    |
|--|---------------------|--------------|--------------|--------------------|----------------------|--------------|--------------|--------------------|----------------------|--------------|--------------|--------------------|
|  | <i>Ucorr</i>        | <i>Lower</i> | <i>Upper</i> | <i>Independent</i> | <i>Ucorr</i>         | <i>Lower</i> | <i>Upper</i> | <i>Independent</i> | <i>Ucorr</i>         | <i>Lower</i> | <i>Upper</i> | <i>Independent</i> |
| Pancake Bonding Distances  |                     |              |              |                    |                      |              |              |                    |                      |              |              |                    |
| S1A ... S1B  | 3.092(2)            | 3.0923       | 3.1059       | 3.0991             | 3.137(5)             | 3.1376       | 3.1725       | 3.155              | 3.159(6)             | 3.1585       | 3.203        | 3.1808             |
| S2A ... S2B  | 3.075(2)            | 3.0752       | 3.0891       | 3.0822             | 3.128(5)             | 3.1281       | 3.1625       | 3.1453             | 3.163(6)             | 3.1625       | 3.2056       | 3.1841             |
| S1C ... S1D  | 3.175(2)            | 3.1742       | 3.1887       | 3.1814             | 3.219(5)             | 3.2194       | 3.2552       | 3.2373             | 3.236(6)             | 3.2356       | 3.2809       | 3.2583             |
| S2C ... S2D  | 3.056(2)            | 3.0566       | 3.072        | 3.0643             | 3.110(5)             | 3.1101       | 3.1494       | 3.1297             | 3.142(6)             | 3.1426       | 3.1911       | 3.1669             |
| Hydrogen Bonding Distances; N <sub>DTDA</sub> ...H-N Angles are provided alongside uncorrected values          |                     |              |              |                    |                      |              |              |                    |                      |              |              |                    |
| N2A ... N3D  | 3.089(6);<br>171.66 | 3.0884       | 3.1034       | 3.0959             | 3.134(10);<br>170.80 | 3.1333       | 3.1694       | 3.1513             | 3.131(14);<br>171.16 | 3.1315       | 3.1829       | 3.1572             |
| N2B ... N3C  | 3.088(6);<br>177.42 | 3.0889       | 3.1054       | 3.0971             | 3.119(10);<br>176.48 | 3.1194       | 3.1608       | 3.1401             | 3.143(14);<br>177.25 | 3.1418       | 3.1958       | 3.1688             |
| Non-Hydrogen Bonding Distances; N <sub>imidazole</sub> ...H-N Angles are provided alongside uncorrected values |                     |              |              |                    |                      |              |              |                    |                      |              |              |                    |
| N4C ... N3B  | 3.431(6);<br>147.74 | 3.4307       | 3.4443       | 3.4375             | 3.491(10);<br>148.07 | 3.4905       | 3.5252       | 3.5079             | 3.497(14);<br>147.71 | 3.4979       | 3.5399       | 3.5189             |
| N4D ... N3A  | 3.576(6);<br>139.39 | 3.5762       | 3.5886       | 3.5824             | 3.602(10);<br>140.30 | 3.6021       | 3.6337       | 3.6179             | 3.630(14);<br>141.13 | 3.631        | 3.6675       | 3.6492             |
| σ-Hole Bonding Distances   |                     |              |              |                    |                      |              |              |                    |                      |              |              |                    |
| S1A ... F6A  | 3.330(4)            | 3.3305       | 3.3521       | 3.3413             | 3.389(7)             | 3.3899       | 3.4496       | 3.4197             | 3.393(8)             | 3.394        | 3.4629       | 3.4284             |
| S2A ... F6A  | 2.904(4)            | 2.9044       | 2.932        | 2.9182             | 2.954(6)             | 2.957        | 3.0294       | 2.9932             | 2.971(8)             | 2.9731       | 3.0609       | 3.017              |
| S1B ... F6B  | 3.177(4)            | 3.1776       | 3.2009       | 3.1893             | 3.244(8)             | 3.2439       | 3.3041       | 3.274              | 3.277(8)             | 3.2772       | 3.3513       | 3.3142             |
| S2B ... F6B  | 3.034(4)            | 3.0345       | 3.0603       | 3.0474             | 3.076(8)             | 3.0766       | 3.1435       | 3.1101             | 3.091(8)             | 3.0923       | 3.175        | 3.1336             |
| S1C ... F5C  | 3.046(4)            | 3.0459       | 3.0745       | 3.0602             | 3.097(8)             | 3.0973       | 3.169        | 3.1332             | 3.128(8)             | 3.1281       | 3.2185       | 3.1733             |
| S2C ... F5C  | 3.318(4)            | 3.3186       | 3.3417       | 3.3301             | 3.374(8)             | 3.3739       | 3.4326       | 3.4033             | 3.406(8)             | 3.4057       | 3.4797       | 3.4427             |
| S1D ... F5D  | 2.969(3)            | 2.9688       | 2.9946       | 2.9817             | 3.026(6)             | 3.0266       | 3.0927       | 3.0597             | 3.048(8)             | 3.0485       | 3.1267       | 3.0876             |
| S2D ... F5D  | 3.182(4)            | 3.1825       | 3.2043       | 3.1934             | 3.243(6)             | 3.2436       | 3.2994       | 3.2715             | 3.277(8)             | 3.2783       | 3.3463       | 3.3123             |

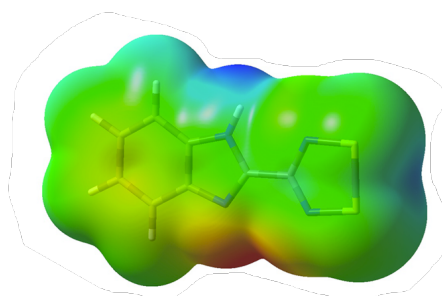


**Figure S3.** Plots of the change in contact distances in F<sub>2</sub>HbimDTDA at variable temperature as determined by the DISTCOR program;<sup>10</sup> the independent model corrected value is represented as a data point and the upper and lower limit models define the height of the error bars.

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Measurements were conducted using a DSC Q2000 apparatus from TA Instruments using hermetically sealed aluminum Tzero pans, also from TA Instruments. Temperature and enthalpy calibrations were confirmed using an indium reference sample. A polycrystalline sample (1.96 mg) and a reference pan were prepared under argon atmosphere. Scans were performed at a range of heating/cooling rates (20, 10, 5, 2, 1, and 0.5 K/min) on the same sample following an initial scan at heating/cooling rate of 20 K. For each rate, temperature was increased first from 193 K to 323 K, then decreased back to 193 K. A 5-minute isotherm was used to verify thermal equilibration at the beginning and end of each sweep. No events were observed in any of the thermograms collected using these parameters.

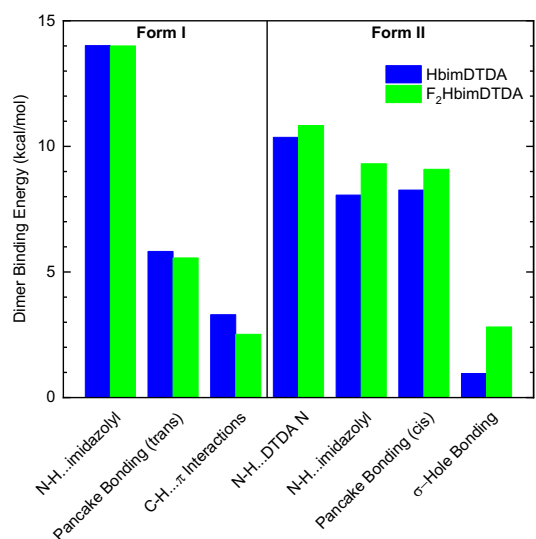
## COMPUTATIONAL ANALYSIS



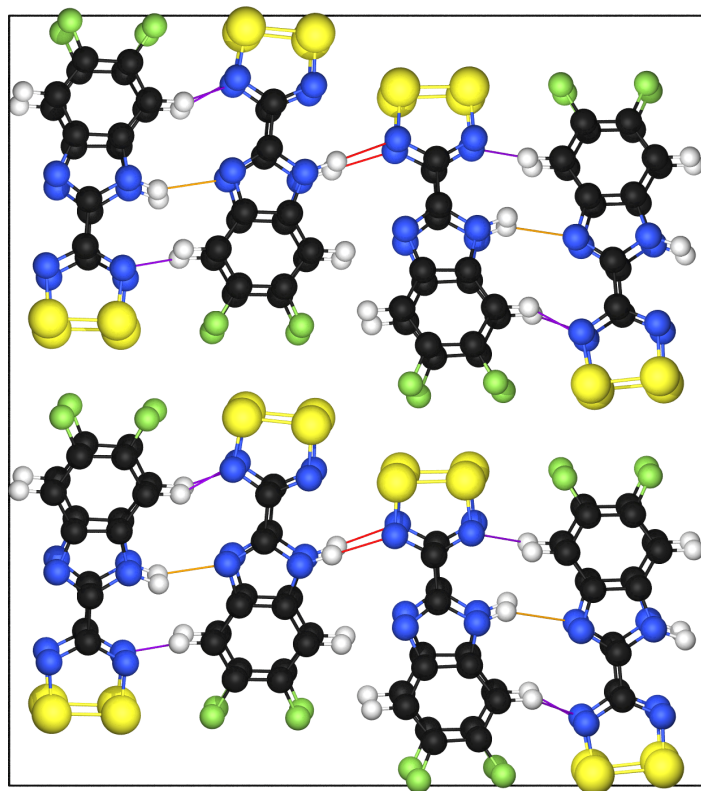
**Figure S4.** Electrostatic surface potential (ESP) map for HbimDTDA depicting the positive potential “ $\sigma$ -hole” between sulfur atoms

**Table S4.** Binding energies, in kcal/mol, for selected molecular dimers of HbimDTDA and F<sub>2</sub>HbimDTDA excised from the optimized molecular crystals. For Form II, there are two non-equivalent sets of dimers within the unit cell; results are shown for the lower-energy dimer of each interaction motif. Results were obtained from gas-phase B3LYP-XDM/pc-2-spd calculations.

| Parameter                             | HbimDTDA | F <sub>2</sub> HbimDTDA |
|---------------------------------------|----------|-------------------------|
| <b>Form I</b>                         |          |                         |
| H-bonding (N-H...imidazolyl)          | -14.01   | -14.00                  |
| Pancake Bonding                       | -5.82    | -5.56                   |
| C-X... $\pi$                          | -3.30    | -2.52                   |
| <b>Form II</b>                        |          |                         |
| H-bonding (Form II) (N-H...DTDA N)    | -10.36   | -10.83                  |
| H-bonding (Form I) (N-H...imidazolyl) | -8.06    | -9.31                   |
| Pancake Bonding                       | -8.26    | -9.09                   |
| $\sigma$ -Hole Bonding                | -0.96    | -2.81                   |



**Figure S5.** Bar graph displaying the binding energies, in kcal/mol, for the molecular dimers of HbimDTDA and F<sub>2</sub>HbimDTDA excised from the optimized molecular crystals. For Form II, there are two non-equivalent sets of dimers within the unit cell; results are shown for the lower-energy dimer of each interaction motif. Results were obtained from gas-phase B3LYP-XDM/pc-2-spd calculations.



**Figure S6.** Excerpt from the crystal structure of F<sub>2</sub>HbimDTDA illustrating the network of intermolecular contacts (purple and orange lines) between nearest *non*-hydrogen bonded neighbors along [001]. Hydrogen bonds are shown as red lines. Note also the proximity of electropositive sulfur atoms to electronegative fluorine atoms.

## REFERENCES

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