

# Expanding Lone Pair··· $\pi$ Interactions to Nonaromatic Systems and Nitrogen Bases: Complexes of $C_2F_3X$ ( $X = F, Cl, Br, I$ ) and TMA(-d<sub>9</sub>)

Yannick Geboes<sup>a,b</sup>, Frank De Proft<sup>b</sup> and Wouter A. Herrebout<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp (Belgium), E-mail: Wouter.herrebout@uantwerpen.be*

<sup>b</sup> *Eenheid Algemene Chemie (ALGC), Member of the QCMM VUB-UGent Alliance Research Group, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels (Belgium)*

## Electronic Supplementary Information

**Table S1:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of C<sub>2</sub>F<sub>4</sub>.

	X	Y	Z
C <sub>2</sub> F <sub>4</sub>			
C	0.316718	0.587967	0.000000
C	-0.316718	-0.587967	0.000000
F	-1.642148	-0.702698	0.000000
F	0.316718	-1.757875	0.000000
F	1.642148	0.702698	0.000000
F	-0.316718	1.757875	0.000000

**Table S2:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of C<sub>2</sub>F<sub>3</sub>Cl.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Cl			
C <sub>2</sub> F <sub>3</sub> Cl			
C	0.000000	0.474053	0.000000
C	-0.672455	-0.686202	0.000000
F	-0.091077	-1.880175	0.000000
F	-1.999532	-0.759966	0.000000
F	-0.676665	1.639573	0.000000
Cl	1.702365	0.604588	0.000000

**Table S3:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of C<sub>2</sub>F<sub>3</sub>Br.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Br			
C	0.000000	0.578257	0.000000
C	1.338899	0.495676	0.000000
F	2.014503	-0.647878	0.000000
F	2.137386	1.558739	0.000000
F	-0.586120	1.795157	0.000000
Br	-1.146438	-0.879936	0.000000

**Table S4:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of C<sub>2</sub>F<sub>3</sub>I.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> I			
C	0.000000	0.895394	0.000000
C	1.289409	1.271052	0.000000
F	2.312902	0.423368	0.000000
F	1.687498	2.539797	0.000000
F	-0.954377	1.858636	0.000000
I	-0.663220	-1.064054	0.000000

**Table S5:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of trimethylamine.

	X	Y	Z
Trimethylamine			
N	0.000000	0.000000	0.410619
C	0.000000	1.379959	-0.066347
H	-0.892330	1.901918	0.309142
H	0.892330	1.901918	0.309142
H	0.000000	1.440847	-1.178318
C	1.195079	-0.689979	-0.066347
H	2.093274	-0.178178	0.309142
H	1.200944	-1.723740	0.309142
H	1.247810	-0.720423	-1.178318
C	-1.195079	-0.689979	-0.066347
H	-1.200944	-1.723740	0.309142
H	-2.093274	-0.178178	0.309142
H	-1.247810	-0.720423	-1.178318

**Table S6:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the N $\cdots\pi$  complex between C<sub>2</sub>F<sub>4</sub> and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>4</sub>			
C	-1.801931	-0.291177	0.000000
C	-1.085165	0.834930	-0.000001
F	-0.716791	1.460715	-1.113179
F	-0.716787	1.460714	1.113177
F	-2.179558	-0.920645	1.113934
F	-2.179562	-0.920644	-1.113933
Trimethylamine			
N	1.686389	-0.189331	-0.000001
C	2.756812	0.804237	-0.000015
H	2.668986	1.441161	-0.892555
H	2.668987	1.441183	0.892510
H	3.766540	0.335983	-0.000010
C	1.772906	-1.021558	-1.196933
H	0.948332	-1.750760	-1.202146
H	1.684252	-0.390221	-2.093412
H	2.733341	-1.580918	-1.253650
C	1.772908	-1.021528	1.196950
H	1.684256	-0.390169	2.093414
H	0.948335	-1.750731	1.202183
H	2.733344	-1.580887	1.253679

**Table S7:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the halogen bonded complex between C<sub>2</sub>F<sub>3</sub>Cl and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Cl			
C	1.848688	0.565730	-0.006706
C	2.712265	-0.460391	0.000331
F	2.345620	-1.739207	-0.001384
F	4.034905	-0.309281	0.009960
F	2.327646	1.829414	-0.004058
Cl	0.146026	0.411278	-0.019041
Trimethylamine			
N	-2.797640	-0.039468	-0.004405
C	-3.674754	1.087346	-0.312929
H	-3.514229	1.892228	0.419360
H	-3.439420	1.475600	-1.314797
H	-4.749924	0.801211	-0.290574
C	-3.081072	-0.544440	1.336882
H	-2.399126	-1.375551	1.570576
H	-2.920703	0.255476	2.074764
H	-4.127424	-0.909884	1.435906
C	-2.980942	-1.103274	-0.988860
H	-2.745993	-0.721860	-1.993558
H	-2.298199	-1.936292	-0.764370
H	-4.022598	-1.494526	-0.995753

**Table S8:** Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the N $\cdots$  $\pi$  complex between C<sub>2</sub>F<sub>3</sub>Cl and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Cl			
C	0.723806	0.995773	-0.450233
C	1.535134	0.225429	0.288012
F	1.769890	0.538744	1.581018
F	0.156211	2.102555	0.014249
F	0.449127	0.767019	-1.727473
Cl	2.276733	-1.210807	-0.269392
Trimethylamine			
N	-1.845187	-0.291088	0.084319
C	-1.926261	-1.477360	-0.764452
H	-2.030983	-1.172765	-1.816220
H	-1.002938	-2.067658	-0.663656
H	-2.789410	-2.127472	-0.497978
C	-1.676040	-0.685631	1.480489
H	-0.757174	-1.282166	1.588635
H	-1.584398	0.211515	2.110895
H	-2.531047	-1.292362	1.853552
C	-3.051579	0.518688	-0.065762
H	-2.971295	1.419878	0.559845
H	-3.158136	0.831392	-1.115017
H	-3.970171	-0.035289	0.230912

**Table S9:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between C<sub>2</sub>F<sub>3</sub>Br and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Br			
C	-1.871658	0.493138	0.000004
C	-2.793545	-0.481349	-0.000003
F	-2.504214	-1.780915	0.000006
F	-4.107730	-0.260063	-0.000019
F	-2.295355	1.781855	-0.000006
Br	-0.023389	0.229736	0.000026
Trimethylamine			
N	2.804891	-0.122529	0.000003
C	3.188330	-0.869845	-1.197024
H	2.688752	-1.849801	-1.195701
H	2.871020	-0.317593	-2.093777
H	4.286654	-1.033285	-1.252866
C	3.189517	-0.861142	1.202040
H	2.873085	-0.302403	2.095078
H	2.689949	-1.841084	1.208316
H	4.287897	-1.024170	1.257984
C	3.433423	1.197823	-0.005096
H	3.116095	1.753779	-0.899574
H	3.116972	1.760257	0.885634
H	4.543246	1.131600	-0.005400

**Table S10:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the N $\cdots$  $\pi$  complex between C<sub>2</sub>F<sub>3</sub>Br and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> Br			
C	0.092482	1.225808	-0.517521
C	1.006428	0.713604	0.319356
F	1.108138	1.206880	1.576026
F	-0.704157	2.237191	-0.191199
F	-0.076426	0.820671	-1.769225
Br	2.131492	-0.705412	-0.089668
Trimethylamine			
N	-2.196447	-0.481178	0.096640
C	-2.065481	-1.724554	-0.658965
H	-2.212303	-1.523120	-1.730364
H	-1.055277	-2.137695	-0.518026
H	-2.806360	-2.491305	-0.339564
C	-1.971835	-0.733258	1.517759
H	-0.964703	-1.152553	1.665177
H	-2.040334	0.211663	2.077402
H	-2.712450	-1.447857	1.941149
C	-3.523294	0.094537	-0.107422
H	-3.604209	1.040932	0.447332
H	-3.674550	0.303648	-1.176771
H	-4.334695	-0.585548	0.235928

**Table S11:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between C<sub>2</sub>F<sub>3</sub>I and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> I			
C	-2.018743	-0.471605	0.000000
C	-2.946698	0.499011	-0.000010
F	-2.661927	1.801554	0.000003
F	-4.263056	0.282977	-0.000036
F	-2.460172	-1.762342	-0.000019
I	0.056658	-0.183454	0.000044
Trimethylamine			
N	2.872324	0.150203	0.000004
C	3.495052	-1.175526	-0.021184
H	3.176312	-1.745443	0.863689
H	3.173015	-1.718455	-0.921693
H	4.603546	-1.109746	-0.022232
C	3.261291	0.874592	1.212342
H	2.765064	1.855854	1.229319
H	2.942910	0.306024	2.098171
H	4.359599	1.030012	1.264549
C	3.256803	0.910905	-1.191342
H	2.935116	0.369320	-2.092748
H	2.760544	1.892193	-1.176836
H	4.354913	1.067926	-1.242916

**Table S12:** Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the N $\cdots$  $\pi$  complex between C<sub>2</sub>F<sub>3</sub>I and trimethylamine.

	X	Y	Z
C <sub>2</sub> F <sub>3</sub> I			
C	-0.427479	1.317701	-0.547708
C	0.531911	0.961501	0.321415
F	0.531437	1.522442	1.559304
F	-1.356208	2.228419	-0.277794
F	-0.519417	0.848572	-1.785614
I	1.989122	-0.460196	-0.045490
Trimethylamine			
N	-2.507759	-0.621448	0.101429
C	-2.273509	-1.876901	-0.607764
H	-2.434505	-1.728009	-1.685748
H	-1.233055	-2.200089	-0.452814
H	-2.949492	-2.689672	-0.259329
C	-2.263485	-0.800378	1.530400
H	-1.224754	-1.127845	1.690481
H	-2.410869	0.155944	2.054396
H	-2.942083	-1.557942	1.982161
C	-3.877985	-0.166458	-0.120355
H	-4.037960	0.789793	0.399184
H	-4.045659	-0.010487	-1.196337
H	-4.629804	-0.898851	0.249997

**Table S13:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_4$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_4</math></b>							
$\nu_1 (\text{A}_g)$	1920.1	0.0	10.3	1923.3	3.2	0.003	11.3
$\nu_2 (\text{A}_g)$	773.9	0.0	11.2	770.6	-3.3	0.4	10.4
$\nu_3 (\text{A}_g)$	389.0	0.0	2.0	388.1	-0.9	2.2	1
$\nu_4 (\text{A}_u)$	201.7	0.0	0.0	210.0	8.3	0.0	0.02
$\nu_5 (\text{B}_{1g})$	1332.0	0.0	0.3	1332.5	0.6	109.8	0.3
$\nu_6 (\text{B}_{1g})$	550.0	0.0	2.1	549.6	-0.4	0.001	1.6
$\nu_7 (\text{B}_{1u})$	416.4	3.8	0.0	418.9	2.6	4.9	0.4
$\nu_8 (\text{B}_{2g})$	525.4	0.0	9.1	511.8	-13.6	6.2	19.2
$\nu_9 (\text{B}_{2u})$	1328.2	409.7	0.0	1317.5	-10.6	232.5	0.2
$\nu_{10} (\text{B}_{2u})$	209.0	4.6	0.0	209.3	0.3	3.7	0.009
$\nu_{11} (\text{B}_{3u})$	1171.1	351.6	0.0	1167.0	-4.1	302.6	0.1
$\nu_{12} (\text{B}_{3u})$	541.6	3.4	0.0	540.8	-0.9	3.6	0.2
<b>TMA</b>							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3111.4	-0.4	29.1	95.8
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2969.1	6.9	175.2	431.7
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1498.2	-0.8	26.1	0.3
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1464.9	0.8	1.3	2.7
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1206.2	2.3	24.0	5.7
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	851.0	-2.0	30.1	10.0
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	385.4	1.6	6.6	1.6
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3159.5	-4.2	5.1	9.4
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1478.0	0.2	0.0	0.002
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1057.5	0.2	0.03	0.008
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	240.6	-3.2	0.0004	0.004
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3163.8	-3.1	26.8	65.2
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3107.2	-3.9	28.7	65.8
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2962.8	7.6	43.8	24.9
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1501.5	0.7	11.1	5.7
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1474.0	-1.1	5.4	8.1
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1421.4	0.4	0.7	1.5
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1303.5	0.1	13.0	1.4
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1114.7	-1.2	6.8	0.5
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1066.1	-0.2	11.6	2.6
$\nu_{21} (\text{E})$	423.6	0.0	0.7	424.8	1.1	3.1	0.5
$\nu_{22} (\text{E})$	290.9	0.4	0.6	286.6	-4.3	0.4	0.5

Van der Waals vibrations:  $9.7 \text{ cm}^{-1}$ ,  $0.0002 \text{ km mol}^{-1}$ ,  $0.03 \text{\AA}^4 \text{amu}^{-1}$ ,  $21.7 \text{ cm}^{-1}$ ,  $0.08 \text{ km mol}^{-1}$ ,  $0.05 \text{\AA}^4 \text{amu}^{-1}$ ,  $31.2 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.02 \text{\AA}^4 \text{amu}^{-1}$ ,  $56.6 \text{ cm}^{-1}$ ,  $0.002 \text{ km mol}^{-1}$ ,  $0.7 \text{\AA}^4 \text{amu}^{-1}$ ,  $69.0 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $0.6 \text{\AA}^4 \text{amu}^{-1}$ ,  $69.5 \text{ cm}^{-1}$ ,  $0.01 \text{ km mol}^{-1}$ ,  $0.5 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S14:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_4$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
$\text{C}_2\text{F}_4$							
$\nu_1 (\text{A}_g)$	1920.1	0.0	10.3	1923.3	3.1	0.005	11.5
$\nu_2 (\text{A}_g)$	773.9	0.0	11.2	770.6	-3.3	0.2	9.7
$\nu_3 (\text{A}_g)$	389.0	0.0	2.0	387.5	-1.4	0.05	1.6
$\nu_4 (\text{A}_u)$	201.7	0.0	0.0	209.9	8.3	0.2	0.04
$\nu_5 (\text{B}_{1g})$	1332.0	0.0	0.3	1332.8	0.8	113.2	0.2
$\nu_6 (\text{B}_{1g})$	550.0	0.0	2.1	549.6	-0.4	0.0008	1.6
$\nu_7 (\text{B}_{1u})$	416.4	3.8	0.0	423.2	6.8	9.6	0.2
$\nu_8 (\text{B}_{2g})$	525.4	0.0	9.1	511.8	-13.6	6.3	19.2
$\nu_9 (\text{B}_{2u})$	1328.2	409.7	0.0	1317.9	-10.3	234.2	0.1
$\nu_{10} (\text{B}_{2u})$	209.0	4.6	0.0	209.4	0.3	3.7	0.03
$\nu_{11} (\text{B}_{3u})$	1171.1	351.6	0.0	1167.5	-3.7	286.7	0.4
$\nu_{12} (\text{B}_{3u})$	541.6	3.4	0.0	540.7	-0.9	3.6	0.2
TMA- $\text{d}_9$							
$\nu_1 (\text{A}_1)$	2286.9	51.7	81.2	2285.9	-1.0	46.5	53.3
$\nu_2 (\text{A}_1)$	2142.3	72.7	232.7	2146.1	3.8	75.3	246.4
$\nu_3 (\text{A}_1)$	1151.7	0.2	5.9	1151.2	-0.5	8.3	4.5
$\nu_4 (\text{A}_1)$	1079.2	12.6	0.2	1078.6	-0.6	15.2	0.2
$\nu_5 (\text{A}_1)$	1018.9	33.5	3.4	1021.4	2.5	35.2	3.4
$\nu_6 (\text{A}_1)$	756.9	12.4	9.6	755.4	-1.5	17.0	8.8
$\nu_7 (\text{A}_1)$	323.0	4.6	0.8	326.0	3.1	6.3	0.8
$\nu_8 (\text{A}_2)$	2345.4	0.0	0.0	2342.2	-3.2	1.7	3.6
$\nu_9 (\text{A}_2)$	1067.7	0.0	0.0	1067.4	-0.3	0.004	0.007
$\nu_{10} (\text{A}_2)$	801.3	0.0	0.0	801.8	0.6	0.001	0.0009
$\nu_{11} (\text{A}_2)$	173.1	0.0	0.0	170.8	-2.3	0.001	0.002
$\nu_{12} (\text{E})$	2349.0	17.4	46.2	2346.6	-2.4	13.9	35.1
$\nu_{13} (\text{E})$	2287.5	8.1	21.2	2287.6	0.1	10.6	25.9
$\nu_{14} (\text{E})$	2135.6	36.1	4.2	2139.6	4.1	33.9	6.3
$\nu_{15} (\text{E})$	1252.4	33.4	1.0	1252.7	0.4	29.9	0.9
$\nu_{16} (\text{E})$	1078.6	2.1	2.4	1078.1	-0.5	4.2	2.4
$\nu_{17} (\text{E})$	1073.1	0.2	0.4	1073.2	0.1	0.5	0.4
$\nu_{18} (\text{E})$	1063.4	1.6	3.7	1062.7	-0.7	0.3	3.4
$\nu_{19} (\text{E})$	886.2	7.4	2.6	886.1	-0.1	6.4	2.4
$\nu_{20} (\text{E})$	839.0	0.03	1.0	838.4	-0.6	0.01	1.2
$\nu_{21} (\text{E})$	352.0	0.007	0.5	351.1	-0.9	0.01	0.5
$\nu_{22} (\text{E})$	210.6	0.2	0.3	207.6	-3.0	0.1	0.3

Van der Waals vibrations:  $8.8 \text{ cm}^{-1}$ ,  $0.0001 \text{ km mol}^{-1}$ ,  $0.04 \text{ \AA}^4 \text{amu}^{-1}$ ,  $19.4 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.04 \text{ \AA}^4 \text{amu}^{-1}$ ,  $28.2 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.01 \text{ \AA}^4 \text{amu}^{-1}$ ,  $53.9 \text{ cm}^{-1}$ ,  $0.002 \text{ km mol}^{-1}$ ,  $0.6 \text{ \AA}^4 \text{amu}^{-1}$ ,  $66.3 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $0.6 \text{ \AA}^4 \text{amu}^{-1}$ ,  $66.8 \text{ cm}^{-1}$ ,  $0.02 \text{ km mol}^{-1}$ ,  $0.4 \text{ \AA}^4 \text{amu}^{-1}$ .

**Table S15:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{Cl}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Cl}</math></b>							
$\nu_1$ ( $A'$ )	1843.6	50.2	13.4	1838.4	-5.3	63.0	12.3
$\nu_2$ ( $A'$ )	1323.6	174.3	0.4	1314.9	-8.8	168.5	0.4
$\nu_3$ ( $A'$ )	1203.3	184.4	0.6	1195.1	-8.1	184.2	0.3
$\nu_4$ ( $A'$ )	1062.6	234.1	1.9	1058.7	-3.9	240.0	0.8
$\nu_5$ ( $A'$ )	687.7	2.1	9.2	683.1	-4.7	0.7	17.7
$\nu_6$ ( $A'$ )	511.3	1.0	1.1	512.0	0.7	0.9	1.5
$\nu_7$ ( $A'$ )	462.5	1.3	2.3	456.6	-5.8	6.7	11.7
$\nu_8$ ( $A'$ )	336.8	1.3	1.9	339.4	2.6	1.1	1.9
$\nu_9$ ( $A'$ )	184.9	2.6	0.4	193.5	8.6	4.1	0.4
$\nu_{10}$ ( $A''$ )	544.5	2.2	5.8	543.1	-1.4	1.4	6.2
$\nu_{11}$ ( $A''$ )	368.9	1.0	0.1	378.0	9.0	1.4	0.2
$\nu_{12}$ ( $A''$ )	172.0	0.1	0.01	179.2	7.1	0.03	0.007
<b>TMA</b>							
$\nu_1$ ( $A_1$ )	3111.8	42.4	235.1	3112.3	0.4	33.2	126.5
$\nu_2$ ( $A_1$ )	2962.3	167.2	390.2	2970.8	8.5	196.0	473.3
$\nu_3$ ( $A_1$ )	1499.0	23.4	0.4	1498.7	-0.4	26.0	0.4
$\nu_4$ ( $A_1$ )	1464.0	1.6	2.3	1464.8	0.8	0.5	6.0
$\nu_5$ ( $A_1$ )	1204.0	24.9	5.6	1207.3	3.4	21.7	8.3
$\nu_6$ ( $A_1$ )	853.0	22.9	12.0	850.9	-2.1	41.8	10.6
$\nu_7$ ( $A_1$ )	383.8	7.6	1.1	389.6	5.8	15.1	1.0
$\nu_8$ ( $A_2$ )	3163.7	0.0	0.0	3162.4	-1.3	1.4	2.9
$\nu_9$ ( $A_2$ )	1477.7	0.0	0.0	1477.6	-0.2	0.004	0.003
$\nu_{10}$ ( $A_2$ )	1057.3	0.0	0.0	1058.0	0.7	0.2	0.001
$\nu_{11}$ ( $A_2$ )	243.9	0.0	0.0	239.4	-4.5	0.0001	0.001
$\nu_{12}$ ( $E$ )	3166.8	34.6	87.1	3165.8	-1.0	28.8	70.0
$\nu_{13}$ ( $E$ )	3111.1	26.1	27.8	3110.8	-0.3	26.2	56.5
$\nu_{14}$ ( $E$ )	2955.2	44.4	18.3	2964.8	9.6	42.1	25.8
$\nu_{15}$ ( $E$ )	1500.8	9.8	5.5	1501.2	0.4	11.6	6.1
$\nu_{16}$ ( $E$ )	1475.1	5.7	8.8	1474.3	-0.8	3.7	8.5
$\nu_{17}$ ( $E$ )	1421.1	0.7	1.6	1421.5	0.5	0.2	1.7
$\nu_{18}$ ( $E$ )	1303.4	14.9	1.7	1303.1	-0.3	13.1	1.4
$\nu_{19}$ ( $E$ )	1115.9	9.1	0.4	1114.9	-1.0	8.1	0.5
$\nu_{20}$ ( $E$ )	1066.2	13.6	2.7	1065.5	-0.7	12.4	2.7
$\nu_{21}$ ( $E$ )	423.6	0.006	0.7	422.6	-1.1	0.03	0.7
$\nu_{22}$ ( $E$ )	290.9	0.4	0.6	286.4	-4.6	0.4	0.6

Van der Waals vibrations:  $0.7 \text{ cm}^{-1}$ ,  $0.01 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $10.6 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.1 \text{\AA}^4 \text{amu}^{-1}$ ,  $18.7 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.5 \text{\AA}^4 \text{amu}^{-1}$ ,  $55.5 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $0.1 \text{\AA}^4 \text{amu}^{-1}$ ,  $67.5 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $67.7 \text{ cm}^{-1}$ ,  $0.5 \text{ km mol}^{-1}$ ,  $1.0 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S16:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{Cl}$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
$\text{C}_2\text{F}_3\text{Cl}$							
$\nu_1 (\text{A}')$	1843.6	50.2	13.4	1838.4	-5.3	63.2	12.4
$\nu_2 (\text{A}')$	1323.6	174.3	0.4	1314.9	-8.8	167.5	0.5
$\nu_3 (\text{A}')$	1203.3	184.4	0.6	1195.2	-8.1	181.6	0.3
$\nu_4 (\text{A}')$	1062.6	234.1	1.9	1058.6	-4.0	239.4	0.7
$\nu_5 (\text{A}')$	687.7	2.1	9.2	683.1	-4.7	0.7	17.7
$\nu_6 (\text{A}')$	511.3	1.0	1.1	512.0	0.7	0.9	1.5
$\nu_7 (\text{A}')$	462.5	1.3	2.3	456.6	-5.9	6.4	11.7
$\nu_8 (\text{A}')$	336.8	1.3	1.9	339.2	2.4	1.3	1.9
$\nu_9 (\text{A}')$	184.9	2.6	0.4	193.4	8.5	4.0	0.4
$\nu_{10} (\text{A}'')$	544.5	2.2	5.8	543.1	-1.4	1.4	6.2
$\nu_{11} (\text{A}'')$	368.9	1.0	0.1	378.1	9.2	1.4	0.2
$\nu_{12} (\text{A}'')$	172.0	0.1	0.01	179.0	7.0	0.03	0.009
TMA- $\text{d}_9$							
$\nu_1 (\text{A}_1)$	2286.9	51.7	81.2	2288.6	1.6	52.6	72.3
$\nu_2 (\text{A}_1)$	2142.3	72.7	232.7	2147.2	4.9	85.5	263.2
$\nu_3 (\text{A}_1)$	1151.7	0.2	5.9	1151.0	-0.7	1.6	7.6
$\nu_4 (\text{A}_1)$	1079.2	12.6	0.2	1079.1	-0.1	12.4	0.2
$\nu_5 (\text{A}_1)$	1018.9	33.5	3.4	1023.0	4.2	42.3	4.5
$\nu_6 (\text{A}_1)$	756.9	12.4	9.6	755.4	-1.5	23.3	8.6
$\nu_7 (\text{A}_1)$	323.0	4.6	0.8	328.9	5.9	10.2	0.8
$\nu_8 (\text{A}_2)$	2345.4	0.0	0.0	2344.5	-0.9	0.4	0.8
$\nu_9 (\text{A}_2)$	1067.7	0.0	0.0	1067.3	-0.5	0.001	0.0001
$\nu_{10} (\text{A}_2)$	801.3	0.0	0.0	802.1	0.8	0.0001	0.0007
$\nu_{11} (\text{A}_2)$	173.1	0.0	0.0	169.9	-3.2	0.0001	0.0006
$\nu_{12} (\text{E})$	2349.0	17.4	46.2	2348.2	-0.8	14.6	37.5
$\nu_{13} (\text{E})$	2287.5	8.1	21.2	2289.4	1.9	7.2	22.5
$\nu_{14} (\text{E})$	2135.6	36.1	4.2	2141.0	5.4	33.2	7.0
$\nu_{15} (\text{E})$	1252.4	33.4	1.0	1251.3	-1.0	31.2	0.9
$\nu_{16} (\text{E})$	1078.6	2.1	2.4	1078.1	-0.5	3.0	2.6
$\nu_{17} (\text{E})$	1073.1	0.2	0.4	1073.4	0.3	0.3	0.4
$\nu_{18} (\text{E})$	1063.4	1.6	3.7	1063.0	-0.5	0.7	3.6
$\nu_{19} (\text{E})$	886.2	7.4	2.6	886.2	0.0	7.0	2.5
$\nu_{20} (\text{E})$	839.0	0.03	1.0	838.4	-0.6	0.01	1.2
$\nu_{21} (\text{E})$	352.0	0.007	0.5	351.3	-0.7	0.01	0.5
$\nu_{22} (\text{E})$	210.6	0.2	0.3	207.4	-3.1	0.2	0.3

Van der Waals vibrations:  $0.7 \text{ cm}^{-1}$ ,  $0.01 \text{ km mol}^{-1}$ ,  $0.3 \text{ \AA}^4 \text{amu}^{-1}$ ,  $9.5 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.1 \text{ \AA}^4 \text{amu}^{-1}$ ,  $16.8 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.5 \text{ \AA}^4 \text{amu}^{-1}$ ,  $52.3 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.1 \text{ \AA}^4 \text{amu}^{-1}$ ,  $64.6 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.4 \text{ \AA}^4 \text{amu}^{-1}$ ,  $64.6 \text{ cm}^{-1}$ ,  $0.3 \text{ km mol}^{-1}$ ,  $0.8 \text{ \AA}^4 \text{amu}^{-1}$ .

**Table S17:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{Cl}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Cl}</math></b>							
$\nu_1 (\text{A}')$	1843.6	50.2	13.4	1847.6	4.0	46.7	13.7
$\nu_2 (\text{A}')$	1323.6	174.3	0.4	1326.7	3.1	142.4	0.4
$\nu_3 (\text{A}')$	1203.3	184.4	0.6	1195.3	-7.9	159.9	0.4
$\nu_4 (\text{A}')$	1062.6	234.1	1.9	1060.7	-1.9	172.2	2.0
$\nu_5 (\text{A}')$	687.7	2.1	9.2	685.6	-2.1	2.5	8.9
$\nu_6 (\text{A}')$	511.3	1.0	1.1	511.4	0.1	0.6	1.0
$\nu_7 (\text{A}')$	462.5	1.3	2.3	461.5	-1.0	1.2	2.1
$\nu_8 (\text{A}')$	336.8	1.3	1.9	335.7	-1.1	1.1	1.5
$\nu_9 (\text{A}')$	184.9	2.6	0.4	184.7	-0.1	1.4	0.3
$\nu_{10} (\text{A}'')$	544.5	2.2	5.8	535.4	-9.1	18.8	18.3
$\nu_{11} (\text{A}'')$	368.9	1.0	0.1	372.8	3.8	0.6	0.2
$\nu_{12} (\text{A}'')$	172.0	0.1	0.01	186.1	14.0	0.7	0.1
<b>TMA</b>							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3111.4	-0.4	29.0	98.3
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2969.4	7.1	175.8	433.1
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1498.0	-1.1	26.0	0.4
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1464.4	0.4	1.6	3.0
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1206.7	2.7	24.0	6.0
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	850.7	-2.3	29.9	10.0
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	389.9	6.1	13.4	0.9
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3158.8	-4.8	9.6	19.7
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1477.8	0.04	0.03	0.01
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1057.3	0.04	0.02	0.01
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	242.3	-1.5	0.01	0.02
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3164.3	-2.6	23.6	57.9
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3107.8	-3.3	27.6	59.3
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2963.0	7.8	44.6	29.0
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1501.3	0.5	11.1	5.9
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1473.6	-1.5	4.3	8.0
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1421.1	0.0	0.4	1.6
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1302.8	-0.6	10.9	1.4
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1114.7	-1.3	8.1	0.5
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1065.5	-0.7	21.1	2.4
$\nu_{21} (\text{E})$	423.6	0.006	0.7	422.5	-1.1	0.04	0.5
$\nu_{22} (\text{E})$	290.9	0.4	0.6	288.7	-2.2	0.4	0.5

Van der Waals vibrations:  $9.7 \text{ cm}^{-1}$ ,  $0.02 \text{ km mol}^{-1}$ ,  $0.08 \text{ \AA}^4 \text{amu}^{-1}$ ,  $34.5 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.2 \text{ \AA}^4 \text{amu}^{-1}$ ,  $46.3 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.3 \text{ \AA}^4 \text{amu}^{-1}$ ,  $55.4 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.6 \text{ \AA}^4 \text{amu}^{-1}$ ,  $68.5 \text{ cm}^{-1}$ ,  $0.04 \text{ km mol}^{-1}$ ,  $0.3 \text{ \AA}^4 \text{amu}^{-1}$ ,  $76.2 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $1.1 \text{ \AA}^4 \text{amu}^{-1}$ .

**Table S18:** MP2/aug-cc-pVDZ vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{Cl}$  and TMA- $\text{d}_9$ , and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
$\text{C}_2\text{F}_3\text{Cl}$							
$\nu_1 (\text{A}')$	1843.6	50.2	13.4	1847.6	3.9	46.7	13.8
$\nu_2 (\text{A}')$	1323.6	174.3	0.4	1327.1	3.5	140.5	0.3
$\nu_3 (\text{A}')$	1203.3	184.4	0.6	1195.6	-7.6	156.4	0.4
$\nu_4 (\text{A}')$	1062.6	234.1	1.9	1059.7	-2.9	154.2	2.0
$\nu_5 (\text{A}')$	687.7	2.1	9.2	685.6	-2.1	2.6	8.9
$\nu_6 (\text{A}')$	511.3	1.0	1.1	511.3	0.0	0.6	1.0
$\nu_7 (\text{A}')$	462.5	1.3	2.3	461.5	-1.0	1.2	2.1
$\nu_8 (\text{A}')$	336.8	1.3	1.9	335.8	-1.0	1.2	1.4
$\nu_9 (\text{A}')$	184.9	2.6	0.4	184.7	-0.2	1.3	0.3
$\nu_{10} (\text{A}''')$	544.5	2.2	5.8	535.4	-9.1	18.9	18.3
$\nu_{11} (\text{A}''')$	368.9	1.0	0.1	375.3	6.3	3.8	0.2
$\nu_{12} (\text{A}''')$	172.0	0.1	0.01	185.9	13.9	0.8	0.1
TMA- $\text{d}_9$							
$\nu_1 (\text{A}_1)$	2286.9	51.7	81.2	2285.7	-1.2	32.2	36.5
$\nu_2 (\text{A}_1)$	2142.3	72.7	232.7	2146.1	3.8	76.6	248.5
$\nu_3 (\text{A}_1)$	1151.7	0.2	5.9	1151.0	-0.7	0.3	5.2
$\nu_4 (\text{A}_1)$	1079.2	12.6	0.2	1078.6	-0.6	11.0	0.9
$\nu_5 (\text{A}_1)$	1018.9	33.5	3.4	1021.9	3.0	35.3	3.7
$\nu_6 (\text{A}_1)$	756.9	12.4	9.6	755.2	-1.6	16.7	8.0
$\nu_7 (\text{A}_1)$	323.0	4.6	0.8	327.5	4.5	6.2	0.8
$\nu_8 (\text{A}_2)$	2345.4	0.0	0.0	2342.0	-3.5	3.2	6.5
$\nu_9 (\text{A}_2)$	1067.7	0.0	0.0	1067.3	-0.4	0.04	0.004
$\nu_{10} (\text{A}_2)$	801.3	0.0	0.0	801.7	0.5	0.002	0.004
$\nu_{11} (\text{A}_2)$	173.1	0.0	0.0	172.0	-1.1	0.008	0.01
$\nu_{12} (\text{E})$	2349.0	17.4	46.2	2346.9	-2.1	12.8	32.5
$\nu_{13} (\text{E})$	2287.5	8.1	21.2	2288.2	0.7	17.6	32.6
$\nu_{14} (\text{E})$	2135.6	36.1	4.2	2139.7	4.2	33.3	7.1
$\nu_{15} (\text{E})$	1252.4	33.4	1.0	1251.5	-0.8	30.3	0.9
$\nu_{16} (\text{E})$	1078.6	2.1	2.4	1078.2	-0.4	3.4	2.2
$\nu_{17} (\text{E})$	1073.1	0.2	0.4	1073.0	-0.1	0.6	0.5
$\nu_{18} (\text{E})$	1063.4	1.6	3.7	1062.7	-0.7	20.6	3.0
$\nu_{19} (\text{E})$	886.2	7.4	2.6	886.0	-0.2	6.2	2.3
$\nu_{20} (\text{E})$	839.0	0.03	1.0	838.2	-0.8	0.01	1.2
$\nu_{21} (\text{E})$	352.0	0.007	0.5	350.8	-1.2	0.02	0.4
$\nu_{22} (\text{E})$	210.6	0.2	0.3	209.1	-1.4	0.2	0.3

Van der Waals vibrations:  $8.8 \text{ cm}^{-1}$ ,  $0.02 \text{ km mol}^{-1}$ ,  $0.1 \text{\AA}^4 \text{amu}^{-1}$ ,  $31.4 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $42.8 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $51.9 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.7 \text{\AA}^4 \text{amu}^{-1}$ ,  $64.8 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $72.3 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $1.1 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S19:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{Br}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Br}</math></b>							
$\nu_1 (\text{A}')$	1827.9	81.1	14.6	1819.1	-8.7	120.2	11.0
$\nu_2 (\text{A}')$	1318.6	166.4	0.7	1305.8	-12.8	164.6	1.1
$\nu_3 (\text{A}')$	1186.2	174.2	0.4	1173.2	-12.9	166.7	1.5
$\nu_4 (\text{A}')$	1029.4	207.2	2.7	1023.2	-6.2	198.3	0.9
$\nu_5 (\text{A}')$	659.6	3.5	7.4	653.9	-5.7	0.9	17.4
$\nu_6 (\text{A}')$	504.0	1.5	1.0	504.4	0.4	1.4	1.2
$\nu_7 (\text{A}')$	371.8	0.5	3.1	357.2	-14.6	9.2	22.1
$\nu_8 (\text{A}')$	313.4	2.5	1.3	313.2	-0.3	3.5	1.5
$\nu_9 (\text{A}')$	161.2	1.6	0.6	171.1	9.9	4.0	1.1
$\nu_{10} (\text{A}''')$	554.1	2.9	4.9	553.7	-0.4	1.9	5.6
$\nu_{11} (\text{A}''')$	359.9	0.5	0.1	370.8	10.9	0.8	0.3
$\nu_{12} (\text{A}''')$	159.3	0.1	0.01	168.0	8.6	0.05	0.01
<b>TMA</b>							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3114.9	3.1	42.9	181.3
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2980.2	17.9	205.0	504.4
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1499.2	0.2	26.1	0.7
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1464.7	0.7	0.0	12.7
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1211.3	7.3	20.7	13.7
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	849.0	-4.0	55.2	10.8
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	398.4	14.7	23.0	1.1
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3164.9	1.3	0.0003	0.0005
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1477.0	-0.7	0.0001	0.001
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1058.6	1.3	0.0001	0.0001
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	236.4	-7.5	0.0	0.0001
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3168.1	1.2	25.4	63.5
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3114.5	3.4	15.0	20.1
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2975.0	19.8	38.3	28.2
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1501.2	0.4	13.0	6.0
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1474.2	-0.9	2.6	8.3
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1421.9	0.9	0.01	1.7
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1302.1	-1.3	9.7	1.2
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1114.5	-1.4	7.6	0.7
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1063.7	-2.6	13.1	2.7
$\nu_{21} (\text{E})$	423.6	0.006	0.7	421.8	-1.8	0.01	0.7
$\nu_{22} (\text{E})$	290.9	0.4	0.6	284.4	-6.6	0.4	0.6

Van der Waals vibrations:  $1.2 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $24.1 \text{ cm}^{-1}$ ,  $0.06 \text{ km mol}^{-1}$ ,  $0.09 \text{\AA}^4 \text{amu}^{-1}$ ,  $27.8 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $75.1 \text{ cm}^{-1}$ ,  $1.1 \text{ km mol}^{-1}$ ,  $0.7 \text{\AA}^4 \text{amu}^{-1}$ ,  $79.8 \text{ cm}^{-1}$ ,  $1.5 \text{ km mol}^{-1}$ ,  $1.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $82.4 \text{ cm}^{-1}$ ,  $0.002 \text{ km mol}^{-1}$ ,  $0.004 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S20:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{Br}$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Br}</math></b>							
$\nu_1$ ( $A'$ )	1827.9	81.1	14.6	1819.1	-8.8	120.7	11.1
$\nu_2$ ( $A'$ )	1318.6	166.4	0.7	1305.8	-12.9	159.8	1.1
$\nu_3$ ( $A'$ )	1186.2	174.2	0.4	1173.2	-12.9	166.7	1.4
$\nu_4$ ( $A'$ )	1029.4	207.2	2.7	1023.1	-6.3	219.4	1.3
$\nu_5$ ( $A'$ )	659.6	3.5	7.4	653.9	-5.7	0.9	17.4
$\nu_6$ ( $A'$ )	504.0	1.5	1.0	504.4	0.4	1.4	1.2
$\nu_7$ ( $A'$ )	371.8	0.5	3.1	357.5	-14.3	5.7	21.0
$\nu_8$ ( $A'$ )	313.4	2.5	1.3	313.0	-0.4	3.6	1.5
$\nu_9$ ( $A'$ )	161.2	1.6	0.6	170.7	9.5	4.0	1.1
$\nu_{10}$ ( $A''$ )	554.1	2.9	4.9	553.7	-0.4	1.9	5.6
$\nu_{11}$ ( $A''$ )	359.9	0.5	0.1	371.5	11.6	0.8	0.3
$\nu_{12}$ ( $A''$ )	159.3	0.1	0.01	167.6	8.3	0.04	0.009
<b>TMA-<math>\text{d}_9</math></b>							
$\nu_1$ ( $A_1$ )	2286.9	51.7	81.2	2292.8	5.8	51.9	89.6
$\nu_2$ ( $A_1$ )	2142.3	72.7	232.7	2152.6	10.4	90.2	265.8
$\nu_3$ ( $A_1$ )	1151.7	0.2	5.9	1149.5	-2.2	4.7	11.9
$\nu_4$ ( $A_1$ )	1079.2	12.6	0.2	1079.6	0.4	17.2	0.3
$\nu_5$ ( $A_1$ )	1018.9	33.5	3.4	1028.2	9.3	21.2	6.6
$\nu_6$ ( $A_1$ )	756.9	12.4	9.6	754.0	-2.9	31.0	8.7
$\nu_7$ ( $A_1$ )	323.0	4.6	0.8	336.5	13.6	19.6	2.1
$\nu_8$ ( $A_2$ )	2345.4	0.0	0.0	2346.4	1.0	0.0	0.0002
$\nu_9$ ( $A_2$ )	1067.7	0.0	0.0	1066.7	-1.1	0.0	0.0005
$\nu_{10}$ ( $A_2$ )	801.3	0.0	0.0	802.5	1.3	0.0	0.0
$\nu_{11}$ ( $A_2$ )	173.1	0.0	0.0	167.7	-5.4	0.0007	0.0003
$\nu_{12}$ ( $E$ )	2349.0	17.4	46.2	2350.1	1.1	12.7	33.7
$\nu_{13}$ ( $E$ )	2287.5	8.1	21.2	2293.6	6.1	4.0	17.7
$\nu_{14}$ ( $E$ )	2135.6	36.1	4.2	2147.0	11.5	30.0	8.4
$\nu_{15}$ ( $E$ )	1252.4	33.4	1.0	1249.0	-3.4	28.9	0.8
$\nu_{16}$ ( $E$ )	1078.6	2.1	2.4	1077.7	-0.9	3.3	2.6
$\nu_{17}$ ( $E$ )	1073.1	0.2	0.4	1073.8	0.6	0.3	0.4
$\nu_{18}$ ( $E$ )	1063.4	1.6	3.7	1062.9	-0.5	0.5	3.3
$\nu_{19}$ ( $E$ )	886.2	7.4	2.6	886.0	-0.2	6.6	2.5
$\nu_{20}$ ( $E$ )	839.0	0.03	1.0	837.6	-1.3	0.001	1.4
$\nu_{21}$ ( $E$ )	352.0	0.007	0.5	350.7	-1.3	0.003	0.5
$\nu_{22}$ ( $E$ )	210.6	0.2	0.3	206.1	-4.4	0.2	0.3

Van der Waals vibrations: 1.1  $\text{cm}^{-1}$ , 0.03  $\text{km mol}^{-1}$ , 0.3  $\text{\AA}^4 \text{amu}^{-1}$ , 22.2  $\text{cm}^{-1}$ , 0.03  $\text{km mol}^{-1}$ , 0.1  $\text{\AA}^4 \text{amu}^{-1}$ , 25.5  $\text{cm}^{-1}$ , 0.01  $\text{km mol}^{-1}$ , 0.4  $\text{\AA}^4 \text{amu}^{-1}$ , 69.7  $\text{cm}^{-1}$ , 0.5  $\text{km mol}^{-1}$ , 0.4  $\text{\AA}^4 \text{amu}^{-1}$ , 74.7  $\text{cm}^{-1}$ , 1.7  $\text{km mol}^{-1}$ , 1.5  $\text{\AA}^4 \text{amu}^{-1}$ , 76.7  $\text{cm}^{-1}$ , 0.0  $\text{km mol}^{-1}$ , 0.002  $\text{\AA}^4 \text{amu}^{-1}$ .

**Table S21:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{Br}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Br}</math></b>							
$\nu_1$ ( $A'$ )	1827.9	81.1	14.6	1831.9	4.0	75.6	15.6
$\nu_2$ ( $A'$ )	1318.6	166.4	0.7	1322.0	3.4	137.2	0.6
$\nu_3$ ( $A'$ )	1186.2	174.2	0.4	1179.0	-7.1	150.9	0.4
$\nu_4$ ( $A'$ )	1029.4	207.2	2.7	1028.2	-1.2	168.4	2.1
$\nu_5$ ( $A'$ )	659.6	3.5	7.4	658.2	-1.4	3.8	7.2
$\nu_6$ ( $A'$ )	504.0	1.5	1.0	504.1	0.1	1.0	0.8
$\nu_7$ ( $A'$ )	371.8	0.5	3.1	372.3	0.5	0.6	2.3
$\nu_8$ ( $A'$ )	313.4	2.5	1.3	312.4	-1.0	2.1	1.0
$\nu_9$ ( $A'$ )	161.2	1.6	0.6	161.4	0.2	1.3	0.5
$\nu_{10}$ ( $A''$ )	554.1	2.9	4.9	544.0	-10.0	20.8	18.2
$\nu_{11}$ ( $A''$ )	359.9	0.5	0.1	364.0	4.1	0.7	0.7
$\nu_{12}$ ( $A''$ )	159.3	0.1	0.01	176.5	17.1	0.2	0.05
<b>TMA</b>							
$\nu_1$ ( $A_1$ )	3111.8	42.4	235.1	3111.4	-0.5	28.6	97.0
$\nu_2$ ( $A_1$ )	2962.3	167.2	390.2	2968.9	6.6	178.6	437.9
$\nu_3$ ( $A_1$ )	1499.0	23.4	0.4	1497.9	-1.2	25.9	0.4
$\nu_4$ ( $A_1$ )	1464.0	1.6	2.3	1464.3	0.2	1.9	3.2
$\nu_5$ ( $A_1$ )	1204.0	24.9	5.6	1206.5	2.6	24.1	6.2
$\nu_6$ ( $A_1$ )	853.0	22.9	12.0	850.7	-2.3	30.1	9.9
$\nu_7$ ( $A_1$ )	383.8	7.6	1.1	389.5	5.8	12.4	0.9
$\nu_8$ ( $A_2$ )	3163.7	0.0	0.0	3158.6	-5.0	9.5	19.7
$\nu_9$ ( $A_2$ )	1477.7	0.0	0.0	1477.6	-0.2	0.03	0.008
$\nu_{10}$ ( $A_2$ )	1057.3	0.0	0.0	1057.3	0.0	0.1	0.01
$\nu_{11}$ ( $A_2$ )	243.9	0.0	0.0	242.4	-1.5	0.02	0.03
$\nu_{12}$ ( $E$ )	3166.8	34.6	87.1	3164.2	-2.7	23.5	57.9
$\nu_{13}$ ( $E$ )	3111.1	26.1	27.8	3107.6	-3.4	27.7	59.4
$\nu_{14}$ ( $E$ )	2955.2	44.4	18.3	2962.5	7.3	44.8	29.9
$\nu_{15}$ ( $E$ )	1500.8	9.8	5.5	1501.1	0.3	10.9	6.0
$\nu_{16}$ ( $E$ )	1475.1	5.7	8.8	1473.5	-1.6	4.1	8.0
$\nu_{17}$ ( $E$ )	1421.1	0.7	1.6	1420.9	-0.2	0.4	1.6
$\nu_{18}$ ( $E$ )	1303.4	14.9	1.7	1302.7	-0.7	10.3	1.4
$\nu_{19}$ ( $E$ )	1115.9	9.1	0.4	1114.6	-1.3	7.6	0.5
$\nu_{20}$ ( $E$ )	1066.2	13.6	2.7	1065.5	-0.8	12.6	2.5
$\nu_{21}$ ( $E$ )	423.6	0.006	0.7	422.5	-1.1	0.04	0.6
$\nu_{22}$ ( $E$ )	290.9	0.4	0.6	288.7	-2.2	0.4	0.5

Van der Waals vibrations:  $12.7 \text{ cm}^{-1}$ ,  $0.02 \text{ km mol}^{-1}$ ,  $0.06 \text{\AA}^4 \text{amu}^{-1}$ ,  $33.3 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $45.6 \text{ cm}^{-1}$ ,  $0.08 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $52.8 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $68.6 \text{ cm}^{-1}$ ,  $0.06 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $77.6 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $1.3 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S22:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{Br}$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{Br}</math></b>							
$\nu_1$ ( $A'$ )	1827.9	81.1	14.6	1831.9	4.0	75.5	15.6
$\nu_2$ ( $A'$ )	1318.6	166.4	0.7	1322.3	3.7	134.1	0.6
$\nu_3$ ( $A'$ )	1186.2	174.2	0.4	1179.4	-6.8	147.8	0.4
$\nu_4$ ( $A'$ )	1029.4	207.2	2.7	1028.1	-1.3	170.2	1.9
$\nu_5$ ( $A'$ )	659.6	3.5	7.4	658.2	-1.4	3.9	7.2
$\nu_6$ ( $A'$ )	504.0	1.5	1.0	504.1	0.1	1.0	0.8
$\nu_7$ ( $A'$ )	371.8	0.5	3.1	372.5	0.7	0.9	2.4
$\nu_8$ ( $A'$ )	313.4	2.5	1.3	312.4	-1.0	2.1	1.0
$\nu_9$ ( $A'$ )	161.2	1.6	0.6	161.4	0.2	1.3	0.5
$\nu_{10}$ ( $A''$ )	554.1	2.9	4.9	544.0	-10.1	20.9	18.2
$\nu_{11}$ ( $A''$ )	359.9	0.5	0.1	366.1	6.2	2.4	0.5
$\nu_{12}$ ( $A''$ )	159.3	0.1	0.01	176.3	16.9	0.2	0.04
<b>TMA-<math>\text{d}_9</math></b>							
$\nu_1$ ( $A_1$ )	2286.9	51.7	81.2	2285.6	-1.3	32.5	35.9
$\nu_2$ ( $A_1$ )	2142.3	72.7	232.7	2145.8	3.5	78.1	251.3
$\nu_3$ ( $A_1$ )	1151.7	0.2	5.9	1150.8	-0.9	0.5	5.4
$\nu_4$ ( $A_1$ )	1079.2	12.6	0.2	1078.5	-0.7	14.8	0.4
$\nu_5$ ( $A_1$ )	1018.9	33.5	3.4	1021.7	2.8	37.2	3.8
$\nu_6$ ( $A_1$ )	756.9	12.4	9.6	755.2	-1.6	16.9	8.0
$\nu_7$ ( $A_1$ )	323.0	4.6	0.8	327.6	4.7	6.3	0.7
$\nu_8$ ( $A_2$ )	2345.4	0.0	0.0	2341.8	-3.6	3.1	6.5
$\nu_9$ ( $A_2$ )	1067.7	0.0	0.0	1067.2	-0.5	0.03	0.004
$\nu_{10}$ ( $A_2$ )	801.3	0.0	0.0	801.7	0.4	0.002	0.005
$\nu_{11}$ ( $A_2$ )	173.1	0.0	0.0	172.0	-1.1	0.01	0.02
$\nu_{12}$ ( $E$ )	2349.0	17.4	46.2	2346.8	-2.2	12.7	32.5
$\nu_{13}$ ( $E$ )	2287.5	8.1	21.2	2288.1	0.6	17.6	32.7
$\nu_{14}$ ( $E$ )	2135.6	36.1	4.2	2139.4	3.9	33.2	7.4
$\nu_{15}$ ( $E$ )	1252.4	33.4	1.0	1251.5	-0.9	29.4	0.9
$\nu_{16}$ ( $E$ )	1078.6	2.1	2.4	1077.9	-0.7	1.9	2.5
$\nu_{17}$ ( $E$ )	1073.1	0.2	0.4	1072.9	-0.3	0.3	0.5
$\nu_{18}$ ( $E$ )	1063.4	1.6	3.7	1062.3	-1.1	1.1	3.3
$\nu_{19}$ ( $E$ )	886.2	7.4	2.6	886.0	-0.2	6.1	2.3
$\nu_{20}$ ( $E$ )	839.0	0.03	1.0	838.1	-0.9	0.009	1.2
$\nu_{21}$ ( $E$ )	352.0	0.007	0.5	350.7	-1.3	0.04	0.4
$\nu_{22}$ ( $E$ )	210.6	0.2	0.3	209.1	-1.4	0.2	0.2

Van der Waals vibrations:  $11.3 \text{ cm}^{-1}$ ,  $0.02 \text{ km mol}^{-1}$ ,  $0.07 \text{\AA}^4 \text{amu}^{-1}$ ,  $30.6 \text{ cm}^{-1}$ ,  $0.08 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $42.0 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $48.6 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $64.8 \text{ cm}^{-1}$ ,  $0.04 \text{ km mol}^{-1}$ ,  $0.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $73.2 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $1.3 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S23:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{I}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{I}</math></b>							
$\nu_1 (\text{A}')$	1805.0	129.7	16.7	1793.0	-12.1	201.3	10.4
$\nu_2 (\text{A}')$	1312.3	157.3	1.4	1294.3	-18.0	145.2	2.2
$\nu_3 (\text{A}')$	1166.5	159.9	0.5	1149.3	-17.3	150.0	3.7
$\nu_4 (\text{A}')$	1004.0	186.5	2.6	996.8	-7.2	164.8	1.2
$\nu_5 (\text{A}')$	645.4	3.6	7.1	639.4	-5.9	0.7	18.4
$\nu_6 (\text{A}')$	500.0	1.7	0.9	500.0	0.0	1.5	1.2
$\nu_7 (\text{A}')$	324.1	0.9	3.8	310.2	-14.0	5.6	18.5
$\nu_8 (\text{A}')$	289.8	3.7	1.3	280.0	-9.8	16.1	10.8
$\nu_9 (\text{A}')$	144.8	1.4	0.8	156.7	11.9	4.8	1.5
$\nu_{10} (\text{A}'')$	553.8	3.5	3.9	553.5	-0.3	2.6	4.5
$\nu_{11} (\text{A}'')$	346.7	0.2	0.1	358.7	12.0	0.3	0.5
$\nu_{12} (\text{A}'')$	147.4	0.1	0.02	160.0	12.6	0.1	0.02
<b>TMA</b>							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3120.4	8.6	39.8	171.9
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2993.2	31.0	203.3	539.2
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1500.3	1.3	26.6	1.2
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1464.2	0.1	1.0	23.0
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1216.4	12.4	16.0	24.7
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	845.8	-7.2	71.9	11.6
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	411.8	28.0	33.6	0.8
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3168.9	5.2	0.004	0.02
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1476.1	-1.7	0.0004	0.005
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1059.2	1.9	0.01	0.003
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	234.5	-9.4	0.0	0.0002
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3172.0	5.2	20.0	53.7
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3120.1	9.1	9.7	16.4
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2989.1	33.9	33.3	32.6
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1501.0	0.2	14.8	5.9
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1474.2	-0.9	1.4	7.8
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1422.3	1.2	0.1	1.7
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1299.2	-4.2	14.6	1.1
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1113.9	-2.0	7.4	0.9
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1059.9	-6.3	13.2	2.9
$\nu_{21} (\text{E})$	423.6	0.006	0.7	421.0	-2.7	0.01	0.7
$\nu_{22} (\text{E})$	290.9	0.4	0.6	285.4	-5.5	0.4	0.8

Van der Waals vibrations:  $1.1 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $33.4 \text{ cm}^{-1}$ ,  $0.08 \text{ km mol}^{-1}$ ,  $0.08 \text{\AA}^4 \text{amu}^{-1}$ ,  $37.5 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $90.3 \text{ cm}^{-1}$ ,  $6.5 \text{ km mol}^{-1}$ ,  $1.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $101.8 \text{ cm}^{-1}$ ,  $1.0 \text{ km mol}^{-1}$ ,  $1.0 \text{\AA}^4 \text{amu}^{-1}$ ,  $104.0 \text{ cm}^{-1}$ ,  $0.005 \text{ km mol}^{-1}$ ,  $0.1 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S24:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{I}$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{I}</math></b>							
$\nu_1$ ( $A'$ )	1805.0	129.7	16.7	1793.0	-12.1	202.1	10.5
$\nu_2$ ( $A'$ )	1312.3	157.3	1.4	1294.4	-17.9	153.2	2.5
$\nu_3$ ( $A'$ )	1166.5	159.9	0.5	1149.3	-17.3	150.4	3.9
$\nu_4$ ( $A'$ )	1004.0	186.5	2.6	996.8	-7.2	168.8	1.3
$\nu_5$ ( $A'$ )	645.4	3.6	7.1	639.4	-6.0	0.7	18.5
$\nu_6$ ( $A'$ )	500.0	1.7	0.9	500.0	0.0	1.4	1.1
$\nu_7$ ( $A'$ )	324.1	0.9	3.8	309.8	-14.3	7.0	18.5
$\nu_8$ ( $A'$ )	289.8	3.7	1.3	279.9	-9.9	17.3	11.4
$\nu_9$ ( $A'$ )	144.8	1.4	0.8	155.2	10.4	4.8	1.6
$\nu_{10}$ ( $A''$ )	553.8	3.5	3.9	553.5	-0.4	2.6	4.5
$\nu_{11}$ ( $A''$ )	346.7	0.2	0.1	361.0	14.3	0.3	0.6
$\nu_{12}$ ( $A''$ )	147.4	0.1	0.02	158.7	11.3	0.1	0.02
<b>TMA-<math>\text{d}_9</math></b>							
$\nu_1$ ( $A_1$ )	2286.9	51.7	81.2	2299.3	12.4	46.2	107.2
$\nu_2$ ( $A_1$ )	2142.3	72.7	232.7	2160.1	17.8	90.9	265.8
$\nu_3$ ( $A_1$ )	1151.7	0.2	5.9	1146.9	-4.8	10.5	17.8
$\nu_4$ ( $A_1$ )	1079.2	12.6	0.2	1080.7	1.4	21.8	0.7
$\nu_5$ ( $A_1$ )	1018.9	33.5	3.4	1034.4	15.5	35.2	14.4
$\nu_6$ ( $A_1$ )	756.9	12.4	9.6	751.9	-5.0	40.8	9.3
$\nu_7$ ( $A_1$ )	323.0	4.6	0.8	348.6	25.6	22.5	0.6
$\nu_8$ ( $A_2$ )	2345.4	0.0	0.0	2349.4	4.0	0.0009	0.004
$\nu_9$ ( $A_2$ )	1067.7	0.0	0.0	1065.7	-2.0	0.0	0.001
$\nu_{10}$ ( $A_2$ )	801.3	0.0	0.0	803.0	1.7	0.0	0.0
$\nu_{11}$ ( $A_2$ )	173.1	0.0	0.0	166.4	-6.7	0.0	0.0001
$\nu_{12}$ ( $E$ )	2349.0	17.4	46.2	2353.3	4.3	10.0	28.4
$\nu_{13}$ ( $E$ )	2287.5	8.1	21.2	2300.2	12.7	2.4	15.9
$\nu_{14}$ ( $E$ )	2135.6	36.1	4.2	2155.2	19.7	25.4	10.5
$\nu_{15}$ ( $E$ )	1252.4	33.4	1.0	1243.4	-9.0	27.0	0.7
$\nu_{16}$ ( $E$ )	1078.6	2.1	2.4	1076.9	-1.6	4.1	2.5
$\nu_{17}$ ( $E$ )	1073.1	0.2	0.4	1073.9	0.7	0.3	0.4
$\nu_{18}$ ( $E$ )	1063.4	1.6	3.7	1062.9	-0.5	0.2	3.1
$\nu_{19}$ ( $E$ )	886.2	7.4	2.6	885.6	-0.6	6.4	2.5
$\nu_{20}$ ( $E$ )	839.0	0.03	1.0	836.4	-2.6	0.02	1.5
$\nu_{21}$ ( $E$ )	352.0	0.007	0.5	349.8	-2.3	0.04	0.4
$\nu_{22}$ ( $E$ )	210.6	0.2	0.3	207.0	-3.5	0.2	0.3

Van der Waals vibrations:  $1.0 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $31.4 \text{ cm}^{-1}$ ,  $0.05 \text{ km mol}^{-1}$ ,  $0.09 \text{\AA}^4 \text{amu}^{-1}$ ,  $35.3 \text{ cm}^{-1}$ ,  $0.01 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $84.7 \text{ cm}^{-1}$ ,  $5.2 \text{ km mol}^{-1}$ ,  $1.0 \text{\AA}^4 \text{amu}^{-1}$ ,  $92.1 \text{ cm}^{-1}$ ,  $1.1 \text{ km mol}^{-1}$ ,  $0.9 \text{\AA}^4 \text{amu}^{-1}$ ,  $94.2 \text{ cm}^{-1}$ ,  $0.01 \text{ km mol}^{-1}$ ,  $0.07 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S25:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{I}$  and TMA and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{I}</math></b>							
$\nu_1$ ( $A'$ )	1805.0	129.7	16.7	1808.9	3.9	121.4	19.3
$\nu_2$ ( $A'$ )	1312.3	157.3	1.4	1316.0	3.7	131.9	1.2
$\nu_3$ ( $A'$ )	1166.5	159.9	0.5	1160.0	-6.5	138.8	0.6
$\nu_4$ ( $A'$ )	1004.0	186.5	2.6	1003.2	-0.8	154.5	1.8
$\nu_5$ ( $A'$ )	645.4	3.6	7.1	644.2	-1.1	3.9	7.0
$\nu_6$ ( $A'$ )	500.0	1.7	0.9	500.1	0.1	1.2	0.8
$\nu_7$ ( $A'$ )	324.1	0.9	3.8	324.7	0.6	0.8	3.2
$\nu_8$ ( $A'$ )	289.8	3.7	1.3	288.8	-1.0	3.8	1.2
$\nu_9$ ( $A'$ )	144.8	1.4	0.8	145.4	0.6	1.2	0.6
$\nu_{10}$ ( $A''$ )	553.8	3.5	3.9	543.6	-10.2	22.9	18.9
$\nu_{11}$ ( $A''$ )	346.7	0.2	0.1	351.8	5.1	0.5	0.3
$\nu_{12}$ ( $A''$ )	147.4	0.1	0.02	167.8	20.4	0.2	0.1
<b>TMA</b>							
$\nu_1$ ( $A_1$ )	3111.8	42.4	235.1	3111.3	-0.5	27.9	93.7
$\nu_2$ ( $A_1$ )	2962.3	167.2	390.2	2968.5	6.3	183.1	447.7
$\nu_3$ ( $A_1$ )	1499.0	23.4	0.4	1497.7	-1.3	26.0	0.3
$\nu_4$ ( $A_1$ )	1464.0	1.6	2.3	1464.1	0.0	2.1	3.6
$\nu_5$ ( $A_1$ )	1204.0	24.9	5.6	1206.5	2.5	24.4	6.4
$\nu_6$ ( $A_1$ )	853.0	22.9	12.0	850.7	-2.4	30.7	10.0
$\nu_7$ ( $A_1$ )	383.8	7.6	1.1	389.5	5.7	11.9	0.9
$\nu_8$ ( $A_2$ )	3163.7	0.0	0.0	3158.5	-5.2	9.1	19.1
$\nu_9$ ( $A_2$ )	1477.7	0.0	0.0	1477.3	-0.4	0.03	0.008
$\nu_{10}$ ( $A_2$ )	1057.3	0.0	0.0	1057.2	0.0	0.1	0.01
$\nu_{11}$ ( $A_2$ )	243.9	0.0	0.0	242.0	-1.9	0.02	0.04
$\nu_{12}$ ( $E$ )	3166.8	34.6	87.1	3164.0	-2.8	23.5	58.5
$\nu_{13}$ ( $E$ )	3111.1	26.1	27.8	3107.5	-3.6	27.9	60.7
$\nu_{14}$ ( $E$ )	2955.2	44.4	18.3	2962.1	6.9	44.7	31.0
$\nu_{15}$ ( $E$ )	1500.8	9.8	5.5	1500.8	0.1	10.5	6.2
$\nu_{16}$ ( $E$ )	1475.1	5.7	8.8	1473.3	-1.8	3.8	7.9
$\nu_{17}$ ( $E$ )	1421.1	0.7	1.6	1420.7	-0.3	0.4	1.7
$\nu_{18}$ ( $E$ )	1303.4	14.9	1.7	1302.6	-0.8	9.1	1.4
$\nu_{19}$ ( $E$ )	1115.9	9.1	0.4	1114.5	-1.5	7.1	0.5
$\nu_{20}$ ( $E$ )	1066.2	13.6	2.7	1065.4	-0.9	11.9	2.4
$\nu_{21}$ ( $E$ )	423.6	0.006	0.7	422.4	-1.2	0.03	0.5
$\nu_{22}$ ( $E$ )	290.9	0.4	0.6	288.6	-2.4	0.2	0.4

Van der Waals vibrations:  $14.8 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.05 \text{\AA}^4 \text{amu}^{-1}$ ,  $34.1 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $44.3 \text{ cm}^{-1}$ ,  $0.09 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $52.7 \text{ cm}^{-1}$ ,  $0.3 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $68.9 \text{ cm}^{-1}$ ,  $0.09 \text{ km mol}^{-1}$ ,  $0.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $78.8 \text{ cm}^{-1}$ ,  $0.1 \text{ km mol}^{-1}$ ,  $1.5 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S26:** MP2/aug-cc-pVDZ-PP vibrational frequencies, in  $\text{cm}^{-1}$ , infrared intensities, in  $\text{km mol}^{-1}$ , and Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , for the  $\text{N}\cdots\pi$  complex of  $\text{C}_2\text{F}_3\text{I}$  and TMA- $\text{d}_9$  and both monomers, as well as the complexation shift  $\Delta\nu$ .

	Monomer			$\text{N}\cdots\pi$ Bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
<b><math>\text{C}_2\text{F}_3\text{I}</math></b>							
$\nu_1$ ( $A'$ )	1805.0	129.7	16.7	1808.9	3.8	121.2	19.3
$\nu_2$ ( $A'$ )	1312.3	157.3	1.4	1316.2	3.9	126.4	1.1
$\nu_3$ ( $A'$ )	1166.5	159.9	0.5	1160.4	-6.1	134.4	1.0
$\nu_4$ ( $A'$ )	1004.0	186.5	2.6	1003.1	-0.9	157.3	1.7
$\nu_5$ ( $A'$ )	645.4	3.6	7.1	644.2	-1.1	3.9	7.0
$\nu_6$ ( $A'$ )	500.0	1.7	0.9	500.1	0.1	1.2	0.8
$\nu_7$ ( $A'$ )	324.1	0.9	3.8	324.2	0.1	1.7	3.6
$\nu_8$ ( $A'$ )	289.8	3.7	1.3	288.8	-1.0	3.4	1.1
$\nu_9$ ( $A'$ )	144.8	1.4	0.8	145.4	0.6	1.2	0.6
$\nu_{10}$ ( $A''$ )	553.8	3.5	3.9	543.5	-10.3	23.0	18.9
$\nu_{11}$ ( $A''$ )	346.7	0.2	0.1	355.8	9.1	1.5	0.4
$\nu_{12}$ ( $A''$ )	147.4	0.1	0.02	167.5	20.1	0.2	0.07
<b>TMA-<math>\text{d}_9</math></b>							
$\nu_1$ ( $A_1$ )	2286.9	51.7	81.2	2285.6	-1.3	34.0	36.2
$\nu_2$ ( $A_1$ )	2142.3	72.7	232.7	2145.5	3.3	80.3	256.6
$\nu_3$ ( $A_1$ )	1151.7	0.2	5.9	1150.6	-1.1	1.8	5.5
$\nu_4$ ( $A_1$ )	1079.2	12.6	0.2	1078.3	-0.9	15.3	0.3
$\nu_5$ ( $A_1$ )	1018.9	33.5	3.4	1021.8	2.9	35.4	3.9
$\nu_6$ ( $A_1$ )	756.9	12.4	9.6	755.2	-1.7	17.4	8.0
$\nu_7$ ( $A_1$ )	323.0	4.6	0.8	328.2	5.2	5.3	0.2
$\nu_8$ ( $A_2$ )	2345.4	0.0	0.0	2341.7	-3.7	3.1	6.2
$\nu_9$ ( $A_2$ )	1067.7	0.0	0.0	1067.0	-0.7	0.03	0.009
$\nu_{10}$ ( $A_2$ )	801.3	0.0	0.0	801.6	0.4	0.004	0.007
$\nu_{11}$ ( $A_2$ )	173.1	0.0	0.0	171.9	-1.2	0.009	0.02
$\nu_{12}$ ( $E$ )	2349.0	17.4	46.2	2346.7	-2.3	12.7	32.9
$\nu_{13}$ ( $E$ )	2287.5	8.1	21.2	2287.9	0.4	17.1	32.5
$\nu_{14}$ ( $E$ )	2135.6	36.1	4.2	2139.1	3.6	32.8	7.8
$\nu_{15}$ ( $E$ )	1252.4	33.4	1.0	1251.3	-1.1	28.5	0.9
$\nu_{16}$ ( $E$ )	1078.6	2.1	2.4	1077.7	-0.9	1.9	2.6
$\nu_{17}$ ( $E$ )	1073.1	0.2	0.4	1072.8	-0.4	0.4	0.5
$\nu_{18}$ ( $E$ )	1063.4	1.6	3.7	1062.2	-1.3	0.9	3.3
$\nu_{19}$ ( $E$ )	886.2	7.4	2.6	885.9	-0.3	6.0	2.2
$\nu_{20}$ ( $E$ )	839.0	0.03	1.0	838.0	-0.9	0.01	1.1
$\nu_{21}$ ( $E$ )	352.0	0.007	0.5	349.7	-2.3	0.3	0.4
$\nu_{22}$ ( $E$ )	210.6	0.2	0.3	209.0	-1.5	0.2	0.2

Van der Waals vibrations:  $13.1 \text{ cm}^{-1}$ ,  $0.03 \text{ km mol}^{-1}$ ,  $0.06 \text{\AA}^4 \text{amu}^{-1}$ ,  $31.7 \text{ cm}^{-1}$ ,  $0.09 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $40.4 \text{ cm}^{-1}$ ,  $0.04 \text{ km mol}^{-1}$ ,  $0.3 \text{\AA}^4 \text{amu}^{-1}$ ,  $48.0 \text{ cm}^{-1}$ ,  $0.3 \text{ km mol}^{-1}$ ,  $0.2 \text{\AA}^4 \text{amu}^{-1}$ ,  $65.1 \text{ cm}^{-1}$ ,  $0.06 \text{ km mol}^{-1}$ ,  $0.4 \text{\AA}^4 \text{amu}^{-1}$ ,  $74.2 \text{ cm}^{-1}$ ,  $0.2 \text{ km mol}^{-1}$ ,  $1.5 \text{\AA}^4 \text{amu}^{-1}$ .

**Table S27:** Experimental vibrational frequencies for the monomer and complexes, as well as experimental complexation shifts ( $\Delta v_{\text{exp}}$ ) and MP2/aug-cc-pVDZ calculated complexation shifts ( $\Delta v_{\text{calc}, N\cdots\pi}$ ), in  $\text{cm}^{-1}$ , for  $N\cdots\pi$  bonded complex ( $N\cdots\pi$ ) of  $\text{C}_2\text{F}_4$  with TMA- $\text{d}_9$  dissolved in LKr at 120 K.

	Assignment	$\nu_{\text{monomer}}$	$\nu_{\text{complex}}$	$\Delta v_{\text{exp}}$	$\Delta v_{\text{calc}, N\cdots\pi}$
$\text{C}_2\text{F}_4$	$\nu_1 + \nu_9$	3196.6	3198.0	1.4	-7.1
	$\nu_1 + \nu_{11}$	3045.3	3048.6	3.3	-0.5
	$\nu_1$	1870.8	1876.0	5.2	3.1
	$\nu_9$	1330.5	1327.5	-3.0	-10.3
	$\nu_{11}$	1179.5	1177.9	-1.6	-3.7
	$\nu_2$	778.1	777.6	-0.5	-3.3
	$\nu_{12}$	554.7	554.3	-0.4	-0.9
	$\nu_6$	549.9	550.3	0.4	-0.4
	$\nu_8$	505.5	500.9	-4.6	-13.6
	$\nu_3$	395.5	395.8	0.3	-1.4
TMA- $\text{d}_9$	$\nu_{12}$	2233.0	2235.5	2.5	-2.4
	$\nu_1$	2182.1	2184.1	2.0	-1.0
	$\nu_{13}$	2182.1	2184.1	2.0	0.1
	$\nu_2$	2029.5	2039.1	9.6	3.8
	$\nu_{14}$	2029.5	2039.1	9.6	4.1
	$\nu_{15}$	1220.9	a		0.4
	$\nu_4$	1063.3	1064.4	1.1	-0.6
	$\nu_{16}$	1062.3	1063.0	0.7	-0.5
	$\nu_{17}$	1055.7	a		0.1
	$\nu_{18}$	1047.7	a		-0.7
	$\nu_5$	1004.0	1007.0	3.0	2.5
	$\nu_{19}$	873.9	873.5	-0.4	-0.1
	$\nu_{20}$	832.8	a		
	$\nu_6$	741.1	739.5	-1.6	-1.5
	$\nu_{21}$	351.1	a		-0.9
	$\nu_7$	314.2	a		3.1
$\nu_{22}$	201.3	a		-3.0	

<sup>a</sup> Complex band has not been observed.

**Table S28:** Experimental vibrational frequencies for the monomer and complexes, as well as experimental complexation shifts ( $\Delta v_{\text{exp}}$ ) and MP2/aug-cc-pVDZ calculated complexation shifts ( $\Delta v_{\text{calc}}$ ), in  $\text{cm}^{-1}$ , for the halogen bonded complex (HalB) and  $\text{N}\cdots\pi$  bonded complex ( $\text{N}\cdots\pi$ ) of  $\text{C}_2\text{F}_3\text{Cl}$  with TMA- $\text{d}_9$ , dissolved in LKr at 120 K.

	Assignment	$v_{\text{monomer}}$	HalB			$\text{N}\cdots\pi$		
			$v_{\text{complex}}$	$\Delta v_{\text{exp}}$	$\Delta v_{\text{calc}}$	$v_{\text{complex}}$	$\Delta v_{\text{exp}}$	$\Delta v_{\text{calc}}$
$\text{C}_2\text{F}_3\text{Cl}$	$v_1$	1795.2	1791.3	-3.9	-5.3	1800.5	5.3	3.9
	$v_1$ ( $^{13}\text{C}$ )	1788.5	<sup>a</sup>		-5.3	<sup>a</sup>		3.9
	$v_2$	1328.1	1321.0	-7.1	-8.8	1331.3	3.2	3.5
	$v_3$	1214.3	<sup>b</sup>		-8.1	<sup>b</sup>		-7.6
		1200.1	1195.4	-4.7		1195.4	-4.7	
	$2\nu_{10}$	1074.8	1073.0	-1.8	-2.8	<sup>b</sup>		-18.3
	$v_4$	1053.7	<sup>b</sup>		-4.0	<sup>b</sup>		-2.9
	$v_5$ ( $^{35}\text{Cl}$ )	691.2	690.7	-0.5	-4.7	690.7	-0.5	-2.1
	$v_5$ ( $^{37}\text{Cl}$ )	689.6	689.1	-0.5	-4.7	689.1	-0.5	-2.1
	$\nu_{10}$	535.0	534.4	-0.6	-1.4	533.1	-1.9	-9.1
	$\nu_6$	516.3	516.7	0.4	0.7	516.0	-0.3	0.0
	$\nu_7$ ( $^{35}\text{Cl}$ )	462.4	458.3	-4.1	-5.9	462.0	-0.4	-1.0
	$\nu_7$ ( $^{37}\text{Cl}$ )	456.5	452.5	-4.0	-5.9	456.3	-0.2	-1.0
	$\nu_8$	338.1	340.4	2.3	2.4	<sup>a</sup>		-1.0
$\nu_9$	189.8	<sup>a</sup>		8.5	<sup>a</sup>		-0.2	
TMA- $\text{d}_9$	$\nu_{12}$	2233.0	2233.8	0.8	-0.8	2233.8	0.8	-2.1
	$\nu_1$	2182.2	2184.5	2.3	1.6	2184.5	2.3	-1.2
	$\nu_{13}$	2182.2	2184.5	2.3	1.9	2184.5	2.3	0.7
	$\nu_2$	2029.5	2033.1	3.6	4.9	2033.1	3.6	3.8
	$\nu_{14}$	2029.5	2033.1	3.6	5.4	2033.1	3.6	4.2
	$\nu_{19} + \nu_{21}$	1226.5	<sup>b</sup>		-0.7	<sup>b</sup>		-1.4
	$\nu_{15}$	1220.8	<sup>b</sup>		-1.0	<sup>b</sup>		-0.8
	$\nu_3$	1139.4	<sup>a</sup>		-0.7	<sup>a</sup>		-0.7
	$\nu_4$	1063.3	<sup>b</sup>		-0.1	<sup>b</sup>		-0.6
	$\nu_{16}$	1062.3	<sup>b</sup>		-0.5	<sup>b</sup>		-0.4
	$\nu_{17}$	1055.7	<sup>b</sup>		0.3	<sup>b</sup>		-0.1
	$\nu_{18}$	1047.7	<sup>b</sup>		-0.5	<sup>b</sup>		-0.7
	$\nu_5$	1004.0	1008.1	4.1	4.2	1008.1	4.1	3.0
	$\nu_{19}$	873.9	873.8	-0.1	0.0	873.8	-0.1	-0.2
	$\nu_{20}$	832.8	<sup>a</sup>		-0.6	<sup>a</sup>		-0.8
	$\nu_6$	741.1	740.5	-0.6	-1.5	740.5	-0.6	-1.6
	$\nu_{21}$	351.1	351.5	0.4	-0.7	351.5	0.4	-1.2
	$\nu_7$	314.2	318.6	4.4	5.9	318.6	4.4	4.5
$\nu_{22}$	201.3	<sup>a</sup>		-3.1	<sup>a</sup>		-1.4	

<sup>a</sup> Complex band has not been observed.

<sup>b</sup> Bands could not be assigned due to overlap with other complex bands.

**Table S29:** Experimental vibrational frequencies, experimental complexation shifts and MP2/aug-cc-pVDZ-PP calculated complexation shifts ( $\Delta v_{\text{calc, HalB}}$ ), in  $\text{cm}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{Br}$  with TMA- $\text{d}_9$  dissolved in LKr at 120 K. For completeness, the MP2/aug-cc-pVDZ-PP calculated complexation shifts of the  $\text{N}\cdots\pi$  bonded complexes ( $\Delta v_{\text{calc, N}\cdots\pi}$ ) are also given.

	Assignment	$\nu_{\text{monomer}}$	$\nu_{\text{complex}}$	$\Delta v_{\text{exp}}$	$\Delta v_{\text{calc, HalB}}$	$\Delta v_{\text{calc, N}\cdots\pi}$
$\text{C}_2\text{F}_3\text{Br}$	$\nu_1$	1781.8	1774.2	-7.6	-8.8	4.0
	$\nu_{4+} \nu_8 / 2\nu_5$	1330.3	1322.0	-10.3		
	$\nu_2$	1319.8	1307.9	-11.9	-12.9	3.7
	$\nu_3$	1197.2	1184.8	-12.4	-12.9	-6.8
		1171.0	1166.3	-4.7		
	$2 \nu_{10}$	1072.6	1071.7	-0.9		
	$\nu_5 + \nu_7$ ( $^{79}\text{Br}$ )	1034.4	1024.3	-10.1	-6.3	-1.3
	$\nu_5 + \nu_7$ ( $^{81}\text{Br}$ )	1033.3	1024.3	-9.0	-6.3	-1.3
	$2\nu_6$	1018.8	1018.5	-0.3	0.8	0.3
	$\nu_4$	1016.6	1006.9	-9.7	-6.3	-1.3
	$\nu_5$	663.9	659.2	-4.7	-5.7	-1.4
	$\nu_{10}$	535.2	534.7	-0.5	-0.4	-10.1
	$\nu_6$	509.1	509.7	0.6	0.4	0.1
	$\nu_7$	365.8	352.6	-13.2	-14.3	0.7
	$\nu_8$	311.1	310.8	-0.3	-0.4	-1.0
	$\nu_9$	162.2	168.7	6.5	9.5	0.2
	TMA- $\text{d}_9$	$\nu_{12}$	2233.0	2235.2	2.2	1.1
$\nu_1$		2182.2	2187.9	5.7	5.8	-1.3
$\nu_{13}$		2182.2	2187.9	5.7	6.1	0.6
$\nu_2$		2029.5	2039.0	9.5	10.4	3.5
$\nu_{14}$		2029.5	2039.0	9.5	11.5	3.9
$\nu_{19+} \nu_{21}$		1226.5	1224.9	-1.6	-1.5	-1.6
$\nu_{15}$		1220.8	1217.7	-3.1	-3.4	-0.9
$\nu_3$		1139.4	<sup>a</sup>		-2.2	-0.9
$\nu_4$		1063.3	1063.1	-0.2	0.4	-0.7
$\nu_{16}$		1062.3	1062.1	-0.2	-0.9	-0.7
$\nu_{17}$		1055.7	<sup>a</sup>		0.6	-0.3
$\nu_{18}$		1047.7	<sup>a</sup>		-0.5	-1.1
$\nu_5$		1004.0	1013.4	9.4	9.3	2.8
$\nu_{19}$		873.9	873.7	-0.2	-0.2	-0.2
$\nu_{20}$		832.8	<sup>a</sup>		-1.3	-0.9
$\nu_6$		741.1	739.2	-1.9	-2.9	-1.6
$\nu_{21}$		351.1	<sup>b</sup>		-1.3	-1.3
$\nu_7$	314.2	328.2	16.0	13.6	4.7	
$\nu_{22}$	201.3	198.8	-3.5	-4.4	-1.4	

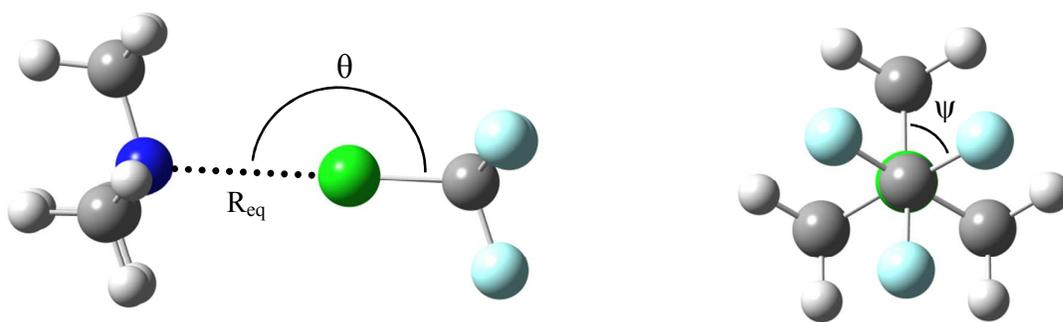
<sup>a</sup> Complex band has not been observed.

<sup>b</sup> Band could not be assigned due to overlap with the  $\nu_7$  complex band of  $\text{C}_2\text{F}_3\text{Br}$ .

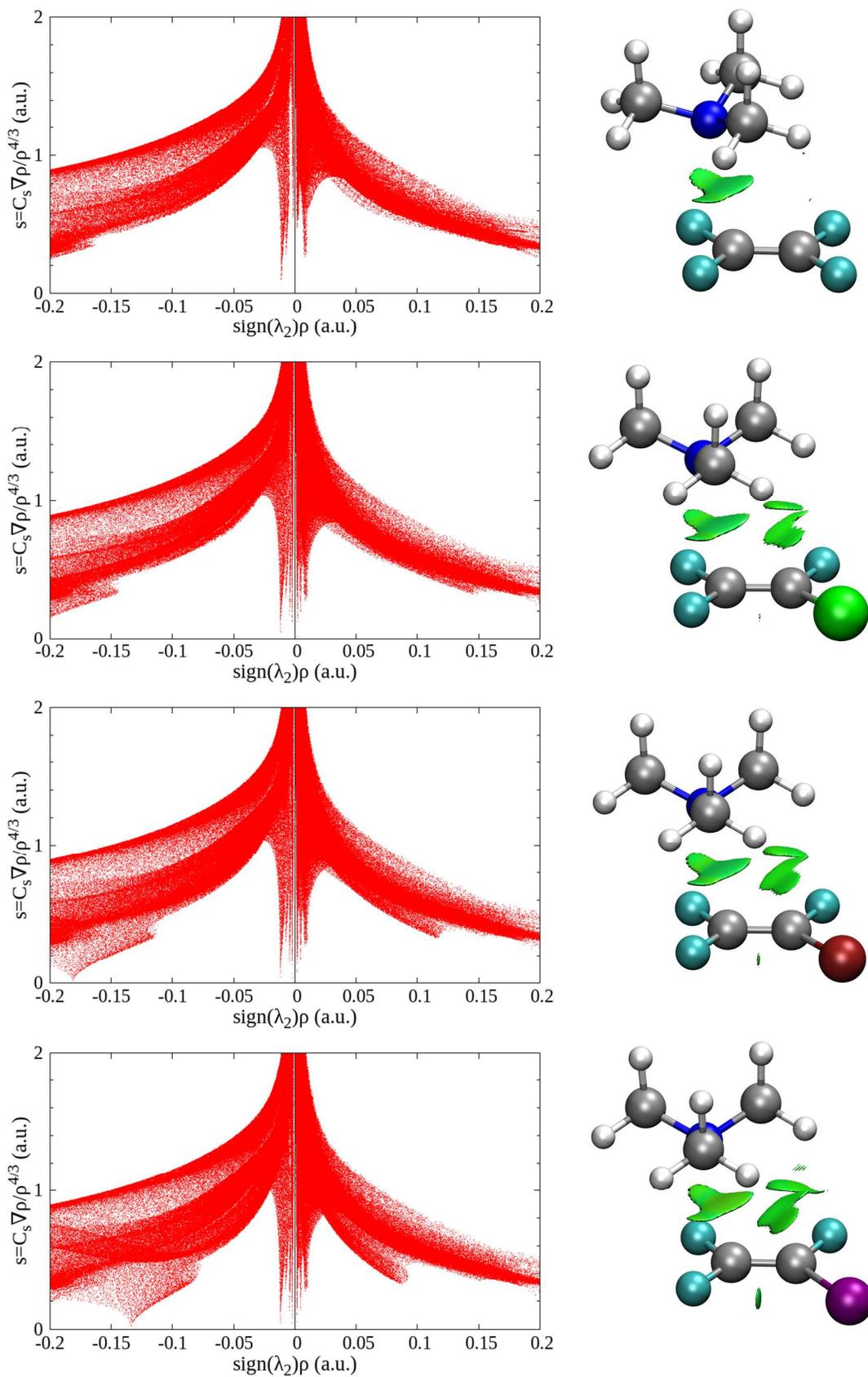
**Table S30:** Experimental vibrational frequencies, experimental complexation shifts and MP2/aug-cc-pVDZ-PP calculated complexation shifts ( $\Delta v_{\text{calc, HalB}}$ ), in  $\text{cm}^{-1}$ , for the halogen bonded complex of  $\text{C}_2\text{F}_3\text{I}$  with TMA- $d_9$  dissolved in LXe at 170 K. For completeness, the MP2/aug-cc-pVDZ-PP calculated complexation shifts of the  $\text{N}\cdots\pi$  bonded complexes ( $\Delta v_{\text{calc, N}\cdots\pi}$ ) are also given.

	Assignment	$v_{\text{monomer}}$	$v_{\text{complex}}$	$\Delta v_{\text{exp}}$	$\Delta v_{\text{calc, HalB}}$	$\Delta v_{\text{calc, N}\cdots\pi}$
$\text{C}_2\text{F}_3\text{I}$	$\nu_1$	1757.8	1746.6	-11.2	-12.1	3.8
	$\nu_1$ ( $^{13}\text{C}$ )	1742.3	1731.4	-10.9	-12.1	3.8
		1732.3	1721.5	-10.8		
		1720.2	1708.8	-11.4		
	$\nu_4 + \nu_7$	1324.6	1304.8	-19.8	-21.6	-0.9
	$\nu_2$	1311.2	1294.9	-16.3	-17.9	3.9
	$2\nu_5$	1301.6	1288.0	-13.6	-11.9	-2.3
	$\nu_3$	1173.9	1158.5	-15.4	-17.3	-6.1
	$\nu_5 + \nu_6$	1155.2	1146.1	-8.9	-6.0	-1.0
	$2\nu_{10}$	1076.4	1074.9	-1.5	-0.7	-20.5
	$2\nu_6$	1012.5	1011.3	-1.2	0.0	0.3
	$\nu_4$	1001.2	995.5	-5.7	-7.2	-0.9
	$\nu_5 + \nu_7$	981.5	<sup>a</sup>		-20.3	-1.1
	$\nu_5 + \nu_8$	972.4	<sup>a</sup>		-15.9	-2.1
	$\nu_5$	651.2	<sup>a</sup>		-6.0	-1.1
	$\nu_{10}$	537.5	536.6	-0.9	-0.4	-10.3
	$\nu_6$	506.4	505.7	-0.7	0.0	0.1
	$\nu_{11}$	348.3	<sup>a</sup>		14.3	9.1
	$\nu_7$	321.1	307.3	-13.8	-14.3	0.1
	$\nu_8$	286.8	276.6	-10.2	-9.9	-1.0
TMA- $d_9$	$\nu_{12}$	2229.9	2234.9	5.0	4.3	-2.3
	$\nu_1$	2179.5	2189.5	10.0	12.4	-1.3
	$\nu_{13}$	2179.5	2189.5	10.0	12.7	0.4
	$\nu_2$	2027.9	2043.8	15.9	17.8	3.3
	$\nu_{14}$	2027.9	2043.8	15.9	19.7	3.6
	$\nu_{19} + \nu_{21}$	1225.2	1222.3	-2.9	-2.9	-2.6
	$\nu_{15}$	1219.9	1208.0	-11.9	-9.0	-1.1
	$\nu_4$	1061.5	1062.2	0.7	1.4	-0.9
	$\nu_{16}$	1061.5	1062.2	0.7	-1.6	-0.9
	$\nu_{18}$	1046.6	<sup>a</sup>		-0.5	-1.3
	$\nu_5$	1002.7	1018.8	16.1	15.5	2.9
	$\nu_{19}$	873.3	872.8	-0.5	-0.6	-0.3
	$\nu_6$	740.5	737.2	-3.3	-5.0	-1.7
	$\nu_{21}$	351.3	349.8	-1.5	-2.3	-0.9
	$\nu_7$	314.5	341.8	27.3	25.6	5.2
$\nu_{22}$	202.5	<sup>a</sup>		-3.5	-1.5	

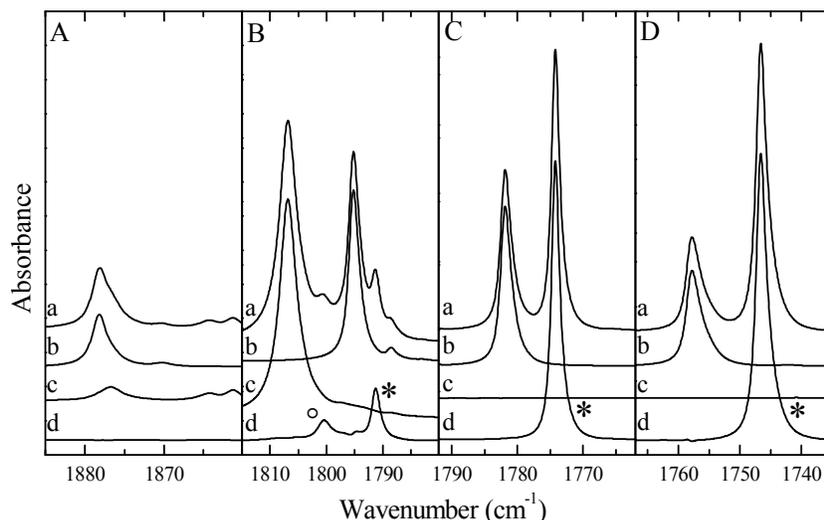
<sup>a</sup> Complex band has not been observed.



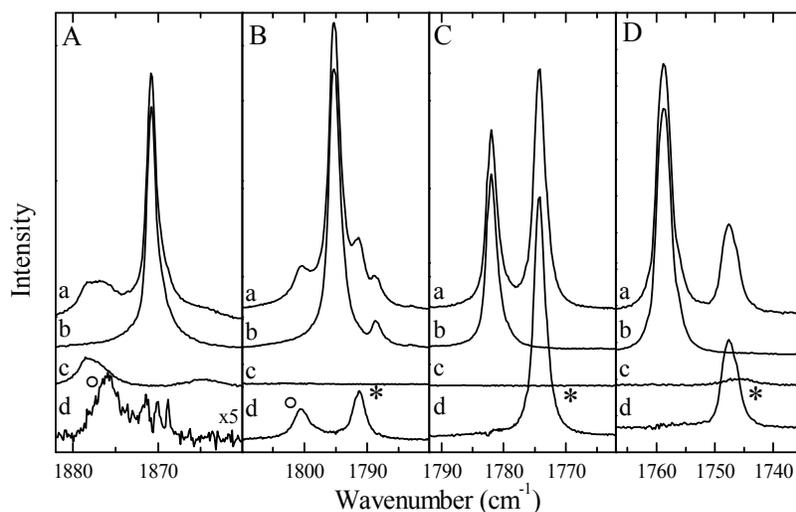
**Figure S1:** MP2/aug-cc-pVDZ(-PP) equilibrium geometries for the halogen bonded complexes of  $\text{CF}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) with trimethylamine.



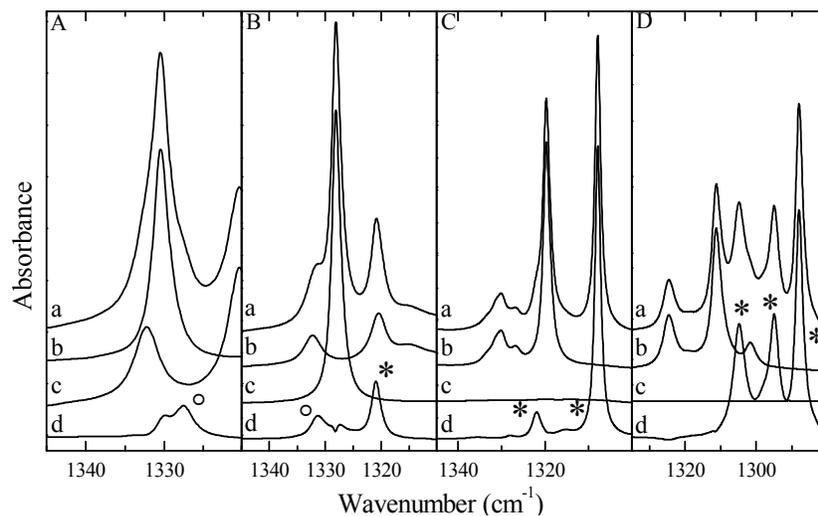
**Figure S2:** Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue (left) and gradient isosurfaces ( $s = 0.5$  a.u., right) for N... $\pi$  bonded species between TMA and  $C_2F_4$  (top),  $C_2F_3Cl$ ,  $C_2F_3Br$  and  $C_2F_3I$  (bottom).



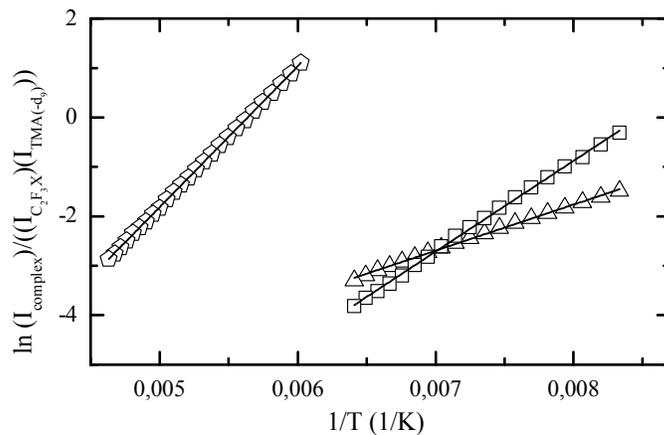
**Figure S3:** Infrared spectra of the  $\nu_{C=C}$  spectral region of  $C_2F_3X$  ( $X = F, Cl, Br, I$ ) for solutions of mixtures of trimethylamine- $d_9$  with  $C_2F_4$  (panel A),  $C_2F_3Cl$  (panel B),  $C_2F_3Br$  (panel C) and  $C_2F_3I$  (panel D) dissolved in LKr at 120 K for panels A-C and LXe at 170 K for panel D. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the solution containing only  $C_2F_3X$  or trimethylamine- $d_9$ , respectively. Trace *d* represents the spectrum of the complex and is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. New bands due to the 1:1  $C(sp^2)-X\cdots N$  halogen bonded and the 1:1 lone pair $\cdots\pi$  bonded complexes are marked with an asterisk (\*) and an open circle ( $^{\circ}$ ), respectively.



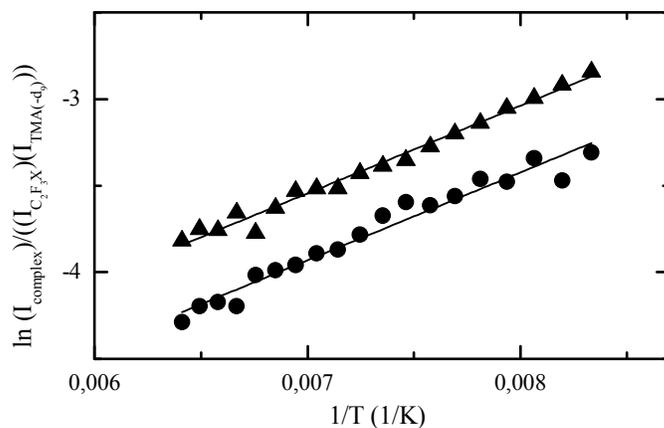
**Figure S4:** Raman spectra of the  $\nu_{C=C}$  spectral region of  $C_2F_3X$  ( $X = F, Cl, Br, I$ ) for solutions of mixtures of trimethylamine- $d_9$  with  $C_2F_4$  (panel A),  $C_2F_3Cl$  (panel B),  $C_2F_3Br$  (panel C) and  $C_2F_3I$  (panel D) dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the solution containing only  $C_2F_3X$  or trimethylamine- $d_9$ , respectively. Trace *d* represents the spectrum of the complex and is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. New bands due to the 1:1  $C(sp^2)-X\cdots N$  halogen bonded and the 1:1 lone pair $\cdots\pi$  bonded complexes are marked with an asterisk (\*) and an open circle ( $^{\circ}$ ), respectively.



**Figure S5:** Infrared spectra of the the antisymmetric CF<sub>2</sub> stretching region of C<sub>2</sub>F<sub>3</sub>X (X = F, Cl, Br, I) for solutions of mixtures of trimethylamine-d<sub>9</sub> with C<sub>2</sub>F<sub>4</sub> (panel A), C<sub>2</sub>F<sub>3</sub>Cl (panel B), C<sub>2</sub>F<sub>3</sub>Br (panel C) and C<sub>2</sub>F<sub>3</sub>I (panel D) dissolved in LKr at 120 K for panels A-C and LXe at 170 K for panel D. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the solution containing only C<sub>2</sub>F<sub>3</sub>X or trimethylamine-d<sub>9</sub>, respectively. Trace *d* represents the spectrum of the complex and is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. New bands due to the 1:1 C(sp<sup>2</sup>)-X⋯N halogen bonded and the 1:1 lone pair⋯π bonded complexes are marked with an asterisk (\*) and an open circle (°), respectively.



**Figure S6:** Typical van 't Hoff plots of the halogen bonded complexes of TMA(-d<sub>9</sub>) with C<sub>2</sub>F<sub>3</sub>Cl (Δ) and C<sub>2</sub>F<sub>3</sub>Br (□) in LKr and C<sub>2</sub>F<sub>3</sub>I (Δ) in LXe.



**Figure S7:** Typical van 't Hoff plots of the lp...π complexes of TMA(-d<sub>9</sub>) with C<sub>2</sub>F<sub>4</sub> (●) and C<sub>2</sub>F<sub>3</sub>Cl (▲) in LKr.