

## Supporting Information

**Table S1** The most positive MEPs on the  $\sigma$ -hole of tetrel atom ( $V_{\max}$ , kcal/mol) in the neutral monomers

	$V_{\max,1}$	$V_{\max,2}$	$V_{\max,3}$	$V_{\max,4}$
<i>p</i> -PyCF <sub>3</sub>	10.58	20.49	20.48	---
<i>p</i> -PySiF <sub>3</sub>	41.56	42.25	42.23	48.38
<i>p</i> -PyGeF <sub>3</sub>	41.57	47.62	55.62	55.64
<i>p</i> -PySiCl <sub>3</sub>	22.17	23.42	25.58	25.51
<i>o</i> -PySiF <sub>3</sub>	34.86	34.86	35.67	21.89
<i>m</i> -PySiF <sub>3</sub>	39.43	35.67	44.86	46.55
$\alpha$ -furanCF <sub>3</sub>	7.38	10.93	10.93	4.97
$\alpha$ -furanSiF <sub>3</sub>	37.96	31.31	31.31	43.82
$\alpha$ -furanGeF <sub>3</sub>	38.96	34.82	34.81	45.91
$\beta$ -furanCF <sub>3</sub>	5.91	10.43	10.38	21.67
$\beta$ -furanSiF <sub>3</sub>	36.21	32.27	32.29	50.25
$\beta$ -furanGeF <sub>3</sub>	36.61	40.31	40.30	58.91

**Table S2** Change of T–X (T = C, Si, and Ge; X = F and Cl) bond length ( $\Delta r$ , Å) in the neutral complexes relative to the isolated molecules

	$\Delta r_1$	$\Delta r_2$	$\Delta r_3$
<i>p</i> -PyCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>1</b> )	-0.001	0.005	0.000
<i>p</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>2</b> )	0.037	0.036	0.036
<i>p</i> -PyGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>3</b> )	0.047	0.044	0.044
<i>p</i> -PySiCl <sub>3</sub> ⋯NH <sub>3</sub> ( <b>4</b> )	0.064	0.071	0.071
<i>o</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>5</b> )	0.036	0.034	0.034
<i>m</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>6</b> )	0.037	0.036	0.035
$\alpha$ -furanCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>7</b> )	-0.004	0.003	0.003
$\alpha$ -furanSiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>8</b> )	0.038	0.034	0.034
$\alpha$ -furanGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>9</b> )	0.046	0.041	0.041
$\beta$ -furanCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>10</b> )	-0.002	0.004	0.000
$\beta$ -furanSiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>11</b> )	0.037	0.034	0.034
$\beta$ -furanGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>12</b> )	0.047	0.043	0.042

**Table S3** Electrostatic energy ( $E^{\text{ele}}$ ), exchange energy ( $E^{\text{ex}}$ ), repulsion energy ( $E^{\text{rep}}$ ), polarization energy ( $E^{\text{pol}}$ ), dispersion energy ( $E^{\text{disp}}$ ), and binding energy ( $E_{\text{b}}$ ) in the neutral complexes. All are in kcal/mol

	$E^{\text{ele}}$	$E^{\text{ex}}$	$E^{\text{rep}}$	$E^{\text{pol}}$	$E^{\text{disp}}$	$E_{\text{b}}$
<i>p</i> -PyCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>1</b> )	-0.56	-2.50	4.28	-0.26	-1.79	-0.83
<i>p</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>2</b> )	-74.80	-82.17	168.31	-36.46	-1.35	-26.47
<i>p</i> -PyGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>3</b> )	-86.21	-88.27	185.48	-39.53	0.17	-28.36
<i>p</i> -PySiCl <sub>3</sub> ⋯NH <sub>3</sub> ( <b>4</b> )	-93.31	-134.98	267.95	-56.80	-8.57	-25.71
<i>o</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>5</b> )	-72.84	-81.10	165.56	-34.87	-1.44	-24.69
<i>m</i> -PySiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>6</b> )	-74.34	-82.08	167.95	-36.04	-1.65	-26.16
$\alpha$ -furanCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>7</b> )	-1.04	-2.04	3.51	-0.17	-1.26	-1.00
$\alpha$ -furanSiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>8</b> )	-75.02	-82.58	169.17	-36.52	-1.39	-26.34
$\alpha$ -furanGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>9</b> )	-85.95	-88.15	185.2	-39.14	0.07	-27.97
$\beta$ -furanCF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>10</b> )	-1.11	-2.99	5.12	-0.33	-1.82	-1.12
$\beta$ -furanSiF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>11</b> )	-71.62	-80.21	163.45	-33.95	-1.63	-23.96
$\beta$ -furanGeF <sub>3</sub> ⋯NH <sub>3</sub> ( <b>12</b> )	-84.44	-87.55	183.37	-38.14	-0.04	-26.81

**Table S4** The most positive MEPs on the  $\sigma$ -hole of tetrel atom ( $V_{\text{max}}$ , kcal/mol) in the protonated monomers

	$V_{\text{max},1}$	$V_{\text{max},2}$	$V_{\text{max},3}$	$V_{\text{max},4}$
H <sup>+</sup> - <i>p</i> -PyCF <sub>3</sub>	85.81(75.23)	114.44	114.35	---
H <sup>+</sup> - <i>p</i> -PySiF <sub>3</sub>	126.03(84.47)	128.93	128.93	132.38
H <sup>+</sup> - <i>p</i> -PyGeF <sub>3</sub>	129.00(87.43)	134.75	134.64	142.13
H <sup>+</sup> - <i>p</i> -PySiCl <sub>3</sub>	92.98(70.81)	107.98	108.00	---
H <sup>+</sup> - <i>o</i> -PySiF <sub>3</sub>	138.50(103.64)	139.92	139.92	145.61
H <sup>+</sup> - <i>m</i> -PySiF <sub>3</sub>	126.62(87.19)	125.64	125.59	134.26
H <sup>+</sup> - $\alpha$ -furanCF <sub>3</sub>	100.38(93.0)	123.24	---	---
H <sup>+</sup> - $\alpha$ -furanSiF <sub>3</sub>	144.27(106.31)	136.42	146.62	153.90
H <sup>+</sup> - $\alpha$ -furanGeF <sub>3</sub>	150.57(111.61)	143.58	149.50	167.17
H <sup>+</sup> - $\beta$ -furanCF	88.86(82.95)	110.95	110.41	119.50
H <sup>+</sup> - $\beta$ -furanSiF <sub>3</sub>	130.12(93.91)	125.89	126.13	143.43
H <sup>+</sup> - $\beta$ -furanGeF <sub>3</sub>	133.99 (97.38)	132.28	132.57	151.15

Note: Data in parentheses are the difference of  $V_{\text{max},1}$  in the protonated molecule relative to the neutral analogue.

**Table S5** Charge transfer (CT, e) and change of charge ( $\Delta q$ , e) on the  $-TX_3$  group in the hydrogen-bonded complexes at the WB97XD/aug-cc-pVDZ level.

	CT	$\Delta q$
$H_3N\cdots H^+ -p\text{-PyCF}_3$ ( <b>13</b> )	0.130	-0.0122 (0.102)
$H_3N\cdots H^+ -p\text{-PySiF}_3$ ( <b>14</b> )	0.127	-0.0120 (0.576)
$H_3N\cdots H^+ -p\text{-PyGeF}_3$ ( <b>15</b> )	0.133	-0.0146 (0.531)
$H_3N\cdots H^+ -p\text{-PySiCl}_3$ ( <b>16</b> )	0.122	-0.0148 (0.547)
$H_3N\cdots H^+ -o\text{-PySiF}_3$ ( <b>17</b> )	0.132	-0.0267 (0.572)
$H_3N\cdots H^+ -m\text{-PySiF}_3$ ( <b>18</b> )	0.128	-0.0138 (0.574)

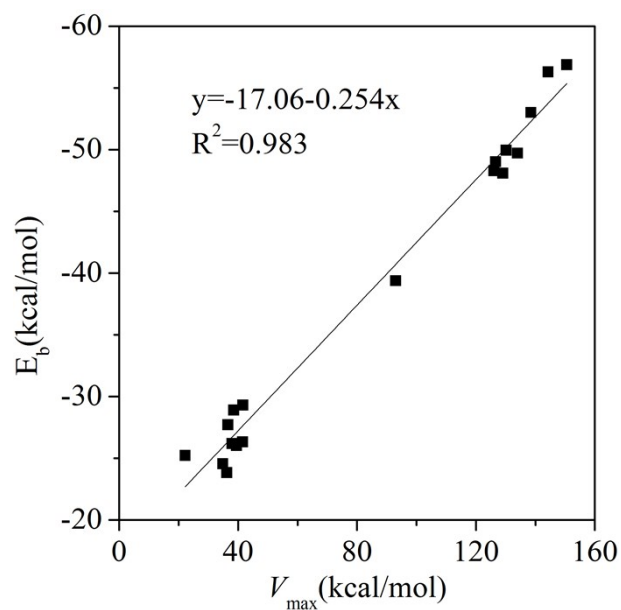
Note: The data in parentheses are the charge on the  $-TX_3$  group in the protonated molecule.

**Table S6** Electron density ( $\rho$ ), Laplacian ( $\nabla^2\rho$ ) and energy density ( $H$ ) at the  $N\cdots H$  BCP in the hydrogen-bonded complexes. All are in au.

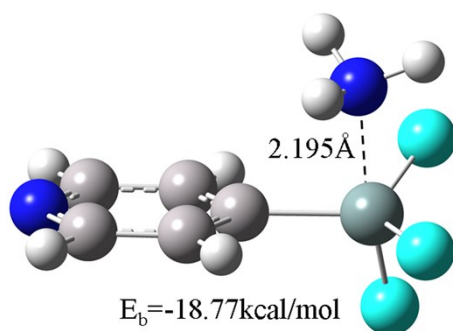
	$\rho$	$\nabla^2\rho$	$H$
$H_3N\cdots H^+ -p\text{-PyCF}_3$ ( <b>13</b> )	0.064	0.067	-0.024
$H_3N\cdots H^+ -p\text{-PySiF}_3$ ( <b>14</b> )	0.062	0.070	-0.022
$H_3N\cdots H^+ -p\text{-PyGeF}_3$ ( <b>15</b> )	0.064	0.067	-0.024
$H_3N\cdots H^+ -p\text{-PySiCl}_3$ ( <b>16</b> )	0.060	0.073	-0.020
$H_3N\cdots H^+ -o\text{-PySiF}_3$ ( <b>17</b> )	0.064	0.069	-0.023
$H_3N\cdots H^+ -m\text{-PySiF}_3$ ( <b>18</b> )	0.062	0.070	-0.022

**Table S7** Electrostatic energy ( $E^{\text{ele}}$ ), exchange energy ( $E^{\text{ex}}$ ), repulsion energy ( $E^{\text{rep}}$ ), polarization energy ( $E^{\text{pol}}$ ), and dispersion energy ( $E^{\text{disp}}$ ) in the hydrogen-bonded complexes. All are in kcal/mol

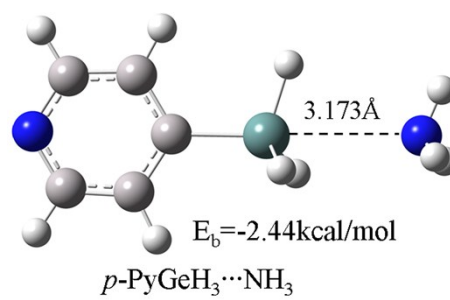
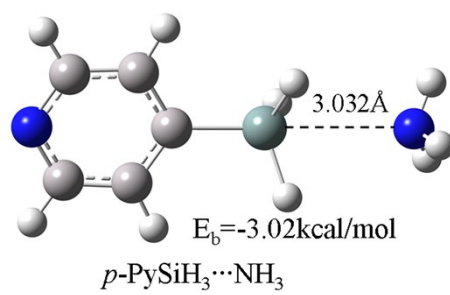
	$E^{\text{ele}}$	$E^{\text{ex}}$	$E^{\text{rep}}$	$E^{\text{pol}}$	$E^{\text{disp}}$
$H_3N\cdots H^+ -p\text{-PyCF}_3$ ( <b>13</b> )	-32.53	-34.12	66.37	-19.31	-4.84
$H_3N\cdots H^+ -p\text{-PySiF}_3$ ( <b>14</b> )	-31.95	-33.51	65.08	-18.70	-4.83
$H_3N\cdots H^+ -p\text{-PyGeF}_3$ ( <b>15</b> )	-33.00	-34.84	67.84	-19.89	-4.60
$H_3N\cdots H^+ -p\text{-PySiCl}_3$ ( <b>16</b> )	-30.80	-32.33	62.60	-17.54	-4.82
$H_3N\cdots H^+ -o\text{-PySiF}_3$ ( <b>17</b> )	-34.59	-37.58	72.53	-20.10	-5.87
$H_3N\cdots H^+ -m\text{-PySiF}_3$ ( <b>18</b> )	-32.00	-33.72	65.46	-18.74	-4.91



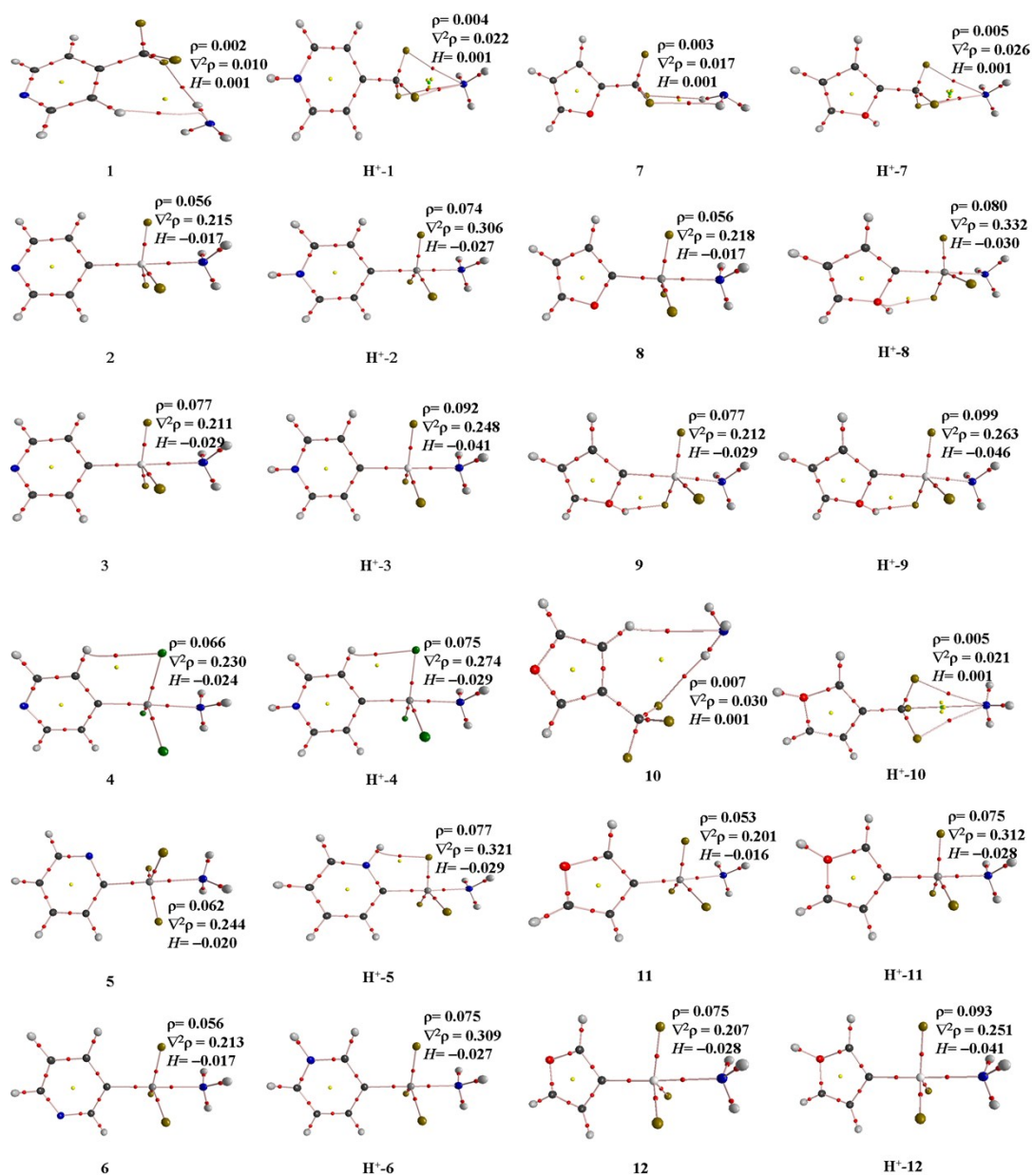
**Fig. S1** Binding energy ( $E_b$ ) versus the most positive MEP ( $V_{\max}$ ) on the C–T (T = Si and Ge) end in the neutral and protonated molecules



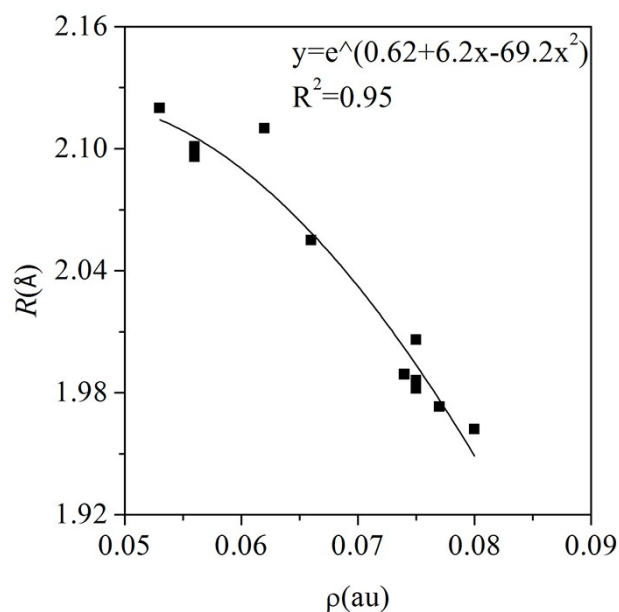
**Fig. S2** Optimized structure of another complex between *p*-PySiF<sub>3</sub> and NH<sub>3</sub>.



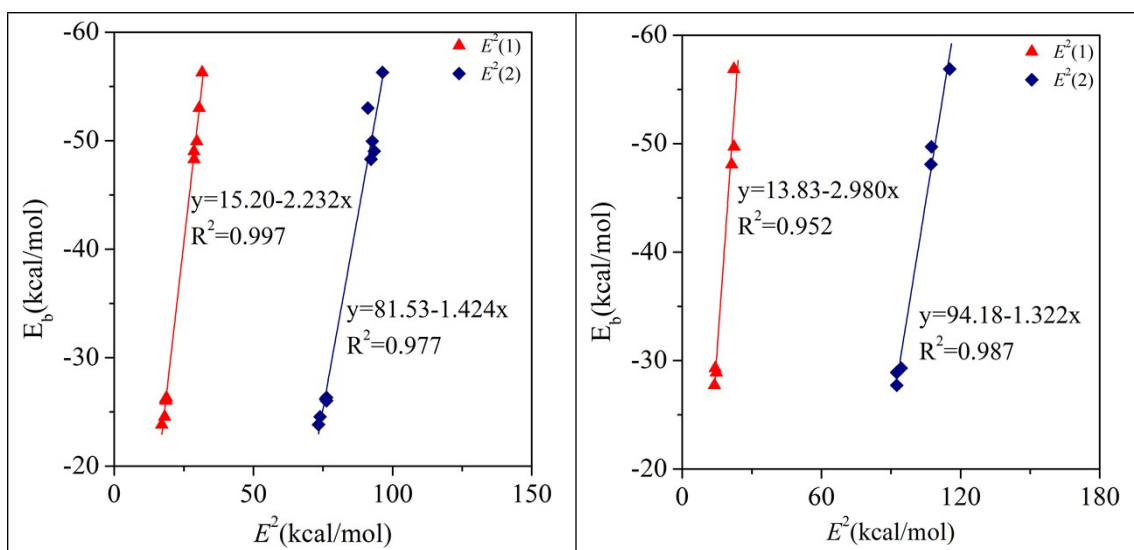
**Fig. S3** Optimized structure of complex between  $p\text{-PyTH}_3$  and  $\text{NH}_3$



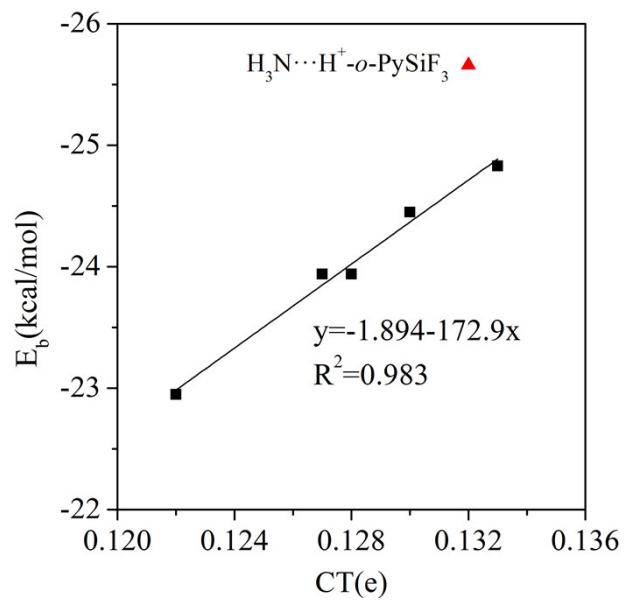
**Fig. S4** Molecular maps of the neutral and the protonated complexes with the electron density ( $\rho$ , au), Laplacian ( $\nabla^2\rho$ , au) and energy density ( $H$ , au) at the intermolecular bond critical point



**Fig. S5** Binding distance ( $R$ ) versus electron density ( $\rho$ ) at the Si...N BCP in the tetrel bond



**Fig. S6** Binding energy ( $E_b$ ) versus second-order perturbation energies ( $E^2$ ) due to the orbital interactions of  $Lp_N \rightarrow BD^*_{C-T}$  (1) and  $Lp_N \rightarrow BD^*_{T-X}$  (2) in the neutral and protonated complexes of furanTF<sub>3</sub> and PyTF<sub>3</sub> (T = Si (left) and Ge (right))



**Fig. S7** Binding energy ( $E_b$ ) versus charge transfer (CT) in the hydrogen-bonded complexes