

Supporting information

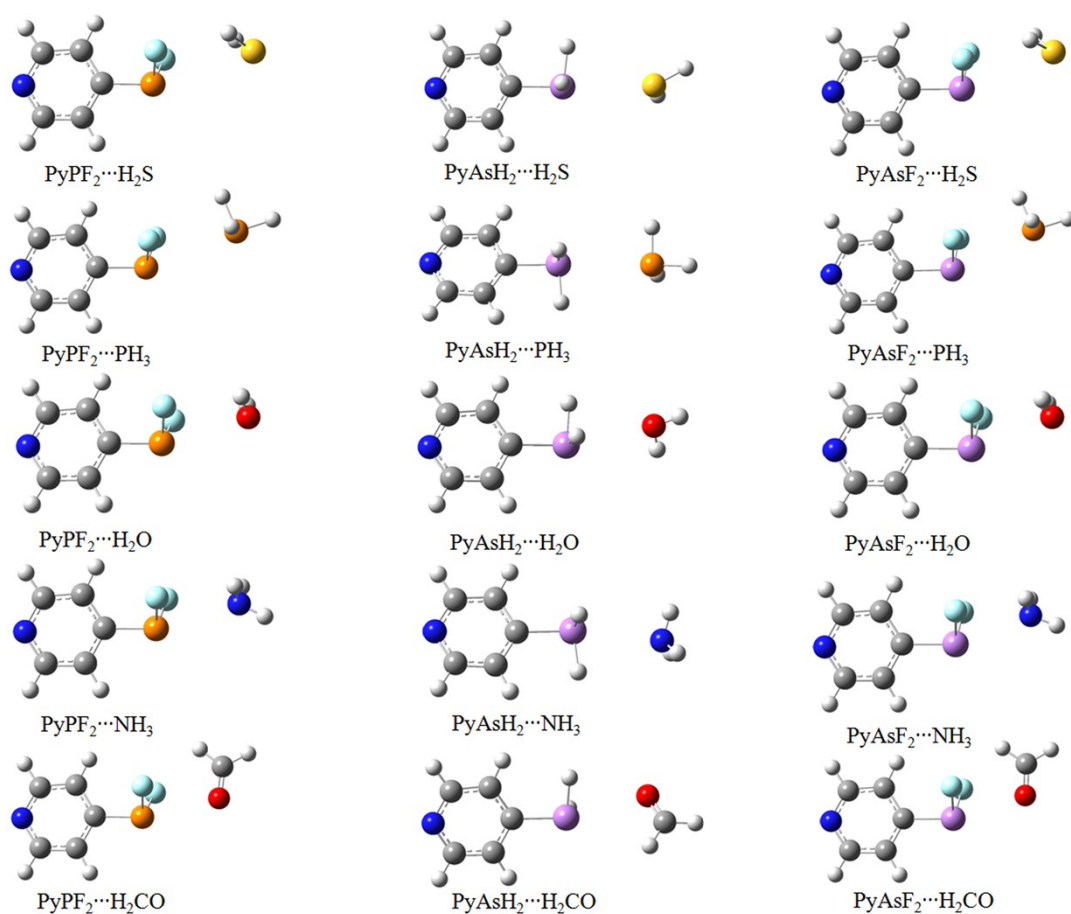


Fig. S1 Optimized structures of PyPF₂, PyAsH₂, and PyAsF₂ complexes with NH₃, H₂O, H₂S, PH₃, and H₂CO.

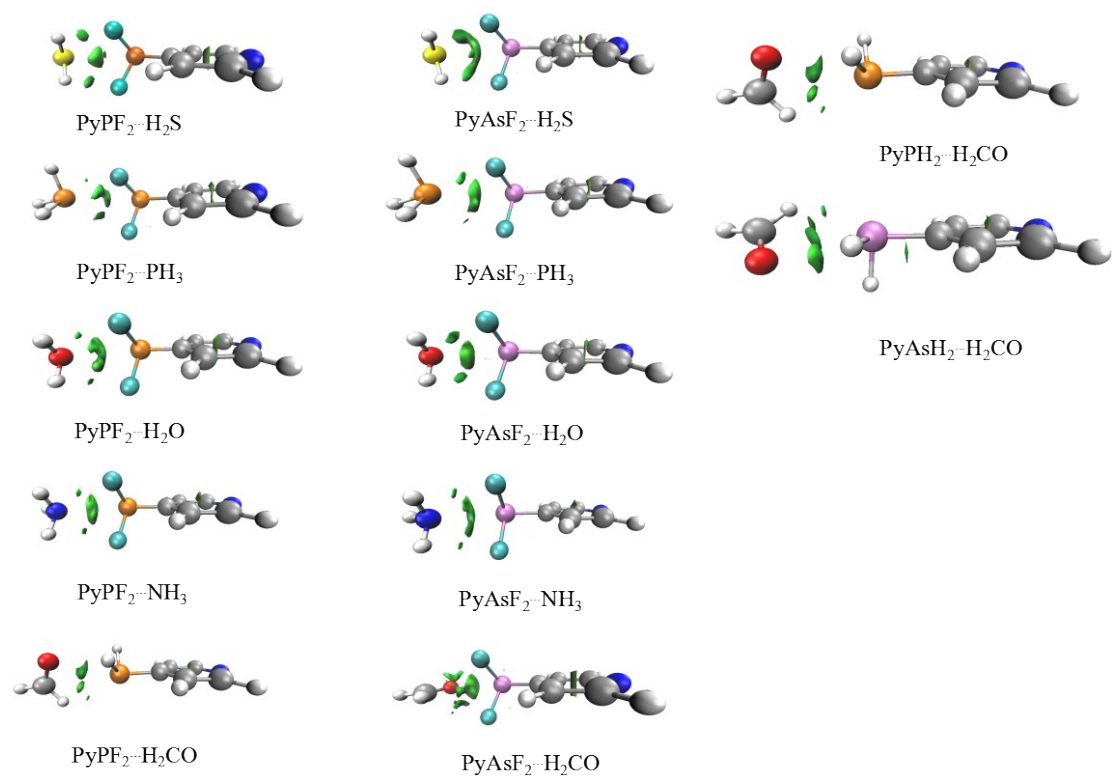


Fig. S2. Gradient isosurfaces of the complexes of PyPH₂...H₂CO, PyAsH₂...H₂CO, and those of PyZF₂ with H₂O, NH₃, H₂S, PH₃, and H₂CO

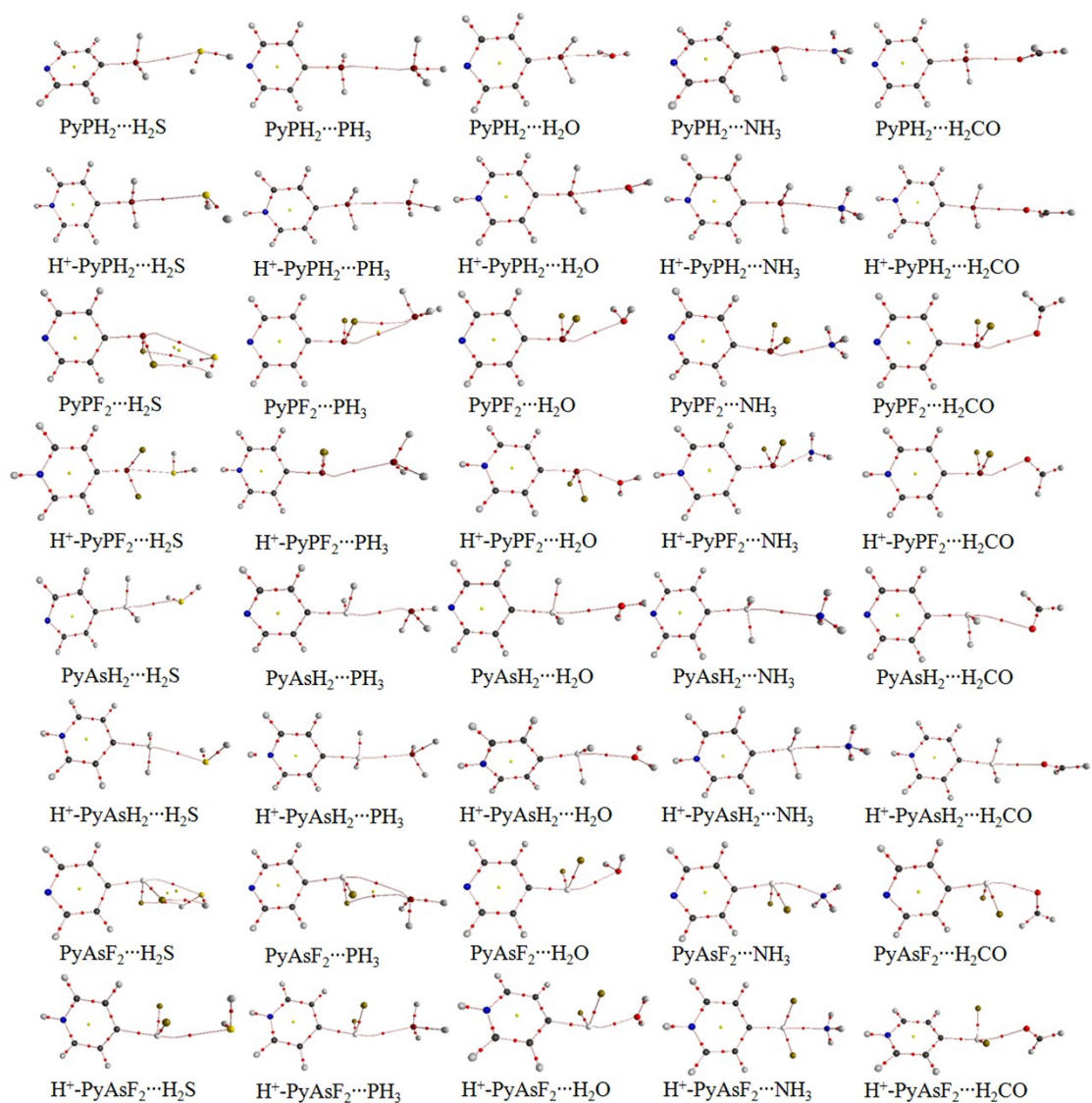


Fig. S3 Molecular maps of pnicogen-bonded complexes. The bond and ring critical points are represented by red and yellow points, respectively.

Table S1 Second-order perturbation energy ($E^{(2)}$, kJ/mol) of the weak secondary interaction in the complexes before and after the protonation on the N atom of pyridine.

No protonation			protonation	
	$E^{(2)}$	type	$E^{(2)}$	type
PyPH ₂ ⋯H ₂ CO	1.8	Lp _P →BD* _{C-H}	0.3	Lp _P →BD* _{C-O}
PyPF ₂ ⋯H ₂ S	1.7	Lp _F →BD* _{S-H}	0.7	Lp _F →BD* _{S-H}
PyPF ₂ ⋯PH ₃	4.4	Lp _F →BD* _{P-H}	2.1	Lp _F →BD* _{P-H}
PyPF ₂ ⋯H ₂ O	0.2	Lp _F →BD* _{O-H}	1.2	Lp _F →BD* _{O-H}
PyPF ₂ ⋯NH ₃	1.5	Lp _F →BD* _{N-H}	5.2	Lp _F →BD* _{N-H}
PyPF ₂ ⋯H ₂ CO	0.5	Lp _F →BD* _{C-H}	2.0	Lp _F →BD* _{C-O}
PyAsH ₂ ⋯H ₂ CO	1.0	Lp _{As} →BD* _{C-H}	0.4	Lp _{As} →BD* _{C-O}
PyAsF ₂ ⋯H ₂ S	3.0	Lp _F →BD* _{S-H}	0.8	Lp _F →BD* _{S-H}
PyAsF ₂ ⋯PH ₃	5.6	Lp _F →BD* _{P-H}	3.8	Lp _F →BD* _{P-H}
PyAsF ₂ ⋯H ₂ O	0.9	Lp _F →BD* _{O-H}	1.4	Lp _F →BD* _{O-H}
PyAsF ₂ ⋯NH ₃	2.0	Lp _F →BD* _{N-H}	7.0	Lp _F →BD* _{N-H}
PyAsF ₂ ⋯H ₂ CO	1.2	Lp _F →BD* _{C-H}	2.3	Lp _F →BD* _{C-O}

Table S2 Second-order perturbation energies ($E^{(2)}$, kJ/mol) of other important orbital interactions in the complexes before and after the protonation on the N atom of pyridine.

No protonation			protonation	
	$E^{(2)}$	type	$E^{(2)}$	type
PyPH ₂ ⋯H ₂ S	3.4	Lp _P →BD* _{S-H}	0.5	Lp _P →BD* _{S-H}
PyPH ₂ ⋯PH ₃	7.5	Lp _P →BD* _{P-H}	2.4	Lp _P →BD* _{P-H}
PyPH ₂ ⋯H ₂ O	2.0	Lp _P →BD* _{O-H}	2.1	Lp _P →BD* _{O-H}
PyPH ₂ ⋯NH ₃	1.9	Lp _P →BD* _{N-H}	1.9	Lp _P →BD* _{N-H}
PyPF ₂ ⋯PH ₃	3.4	Lp _P →BD* _{P-H}	2.3	Lp _P →BD* _{P-H}
PyPF ₂ ⋯NH ₃	0.5	Lp _P →BD* _{N-H}	2.8	Lp _P →BD* _{N-H}
PyAsH ₂ ⋯H ₂ S	3.6	Lp _{As} →BD* _{S-H}	0.4	Lp _{As} →BD* _{S-H}
PyAsH ₂ ⋯PH ₃	7.5	Lp _{As} →BD* _{P-H}	2.6	Lp _{As} →BD* _{P-H}
PyAsH ₂ ⋯H ₂ O	2.3	Lp _{As} →BD* _{O-H}	2.5	Lp _{As} →BD* _{O-H}
PyAsH ₂ ⋯NH ₃	1.8	Lp _{As} →BD* _{N-H}	1.9	Lp _{As} →BD* _{N-H}
PyAsF ₂ ⋯PH ₃	2.3	Lp _{As} →BD* _{P-H}	1.5	Lp _{As} →BD* _{P-H}
PyAsF ₂ ⋯NH ₃	1.0	Lp _{As} →BD* _{N-H}	1.7	Lp _{As} →BD* _{N-H}

Table S3 The most negative MEP (V_{\min} , kJ/mol) on the Lewis base atom in NH₃, H₂O, H₂S, PH₃, and H₂CO as well as the most positive MEP (V_{\max} , kJ/mol) on the pnictogen atom in the protonated molecules

	V_{\min}		V_{\max}
H ₂ S	-74.7	H ⁺ -PyPH ₂	412.4
PH ₃	-77.6	H ⁺ -PyPF ₂	428.8
H ₂ O	-149.1	H ⁺ -PyAsH ₂	414.9
NH ₃	-165.5	H ⁺ -PyAsF ₂	445.6
H ₂ CO	-146.4	---	---

Table S4 Exchange (EX) and repulsion (REP) contributions to the interaction energy in the complexes. All energies are in kJ/mol.

Systems	EX	REP
PyPH ₂ ⋯H ₂ S	-25.7(-40.6)	42.6(70.8)
PyPH ₂ ⋯PH ₃	-34.2(-47.9)	56.3(82.9)
PyPH ₂ ⋯H ₂ O	-20.6(-36.7)	35.0(64.2)
PyPH ₂ ⋯NH ₃	-32.7(-79.5)	54.0(141.0)
PyPH ₂ ⋯H ₂ CO	-33.8(-36.2)	56.7(63.6)
PyPF ₂ ⋯H ₂ S	-22.5(-57.8)	38.4(104.8)
PyPF ₂ ⋯PH ₃	-21.5(-60.3)	36.4(109.3)
PyPF ₂ ⋯H ₂ O	-27.6(-49.3)	49.2(92.5)
PyPF ₂ ⋯NH ₃	-47.0(-192.5)	81.1(366.6)
PyPF ₂ ⋯H ₂ CO	-32.6(-74.1)	56.1(136.1)
PyAsH ₂ ⋯H ₂ S	-27.4 (-46.9)	45.6(82.6)
PyAsH ₂ ⋯PH ₃	-35.6(-56.4)	59.1(99.3)
PyAsH ₂ ⋯H ₂ O	-23.0(-44.4)	38.8(78.8)
PyAsH ₂ ⋯NH ₃	-40.6(-96.2)	67.6(173.6)
PyAsH ₂ ⋯H ₂ CO	-37.7(-45.1)	63.6(80.2)
PyAsF ₂ ⋯H ₂ S	-36.4(-79.8)	62.9(148.7)
PyAsF ₂ ⋯PH ₃	-34.8(-90.2)	60.0(168.8)
PyAsF ₂ ⋯H ₂ O	-47.2(-84.7)	83.8(157.5)
PyAsF ₂ ⋯NH ₃	-79.2(-245.7)	140.8(482.6)
PyAsF ₂ ⋯H ₂ CO	-50.3(-94.1)	88.3(176.2)

Note: Data in parentheses are from the protonated complexes.

Table S5 Electron density (ρ , au), Laplacian ($\nabla^2\rho$, au), and energy density (H , au) at the intermolecular BCP in the protonated complexes

	ρ	$\nabla^2\rho$	H
H ⁺ -PyPH ₂ ⋯H ₂ S	0.0110(0.0032)	0.0301	0.0007
H ⁺ -PyPH ₂ ⋯PH ₃	0.0116(0.0025)	0.0274	0.0004
H ⁺ -PyPH ₂ ⋯H ₂ O	0.0130(0.0051)	0.0520	0.0018
H ⁺ -PyPH ₂ ⋯NH ₃	0.0191(0.0099)	0.0527	0.0003
H ⁺ -PyPH ₂ ⋯H ₂ CO	0.0129(0.0028)	0.0543	0.0019
H ⁺ -PyPF ₂ ⋯H ₂ S	0.0149(0.0101)	0.0314	0.0000
H ⁺ -PyPF ₂ ⋯PH ₃	0.0143(0.0088)	0.0263	-0.0001
H ⁺ -PyPF ₂ ⋯H ₂ O	0.0184(0.0099)	0.0615	0.0012
H ⁺ -PyPF ₂ ⋯NH ₃	0.0393(0.0276)	0.0581	-0.0069
H ⁺ -PyPF ₂ ⋯H ₂ CO	0.0228(0.0126)	0.0661	0.0001
H ⁺ -PyAsH ₂ ⋯H ₂ S	0.0120(0.0039)	0.0299	0.0005
H ⁺ -PyAsH ₂ ⋯PH ₃	0.0128(0.0035)	0.0275	0.0002
H ⁺ -PyAsH ₂ ⋯H ₂ O	0.0145(0.0061)	0.0553	0.0018
H ⁺ -PyAsH ₂ ⋯NH ₃	0.0214(0.0110)	0.0570	0.0001
H ⁺ -PyAsH ₂ ⋯H ₂ CO	0.0145(0.0038)	0.0570	0.0019
H ⁺ -PyAsF ₂ ⋯H ₂ S	0.0188(0.0118)	0.0334	-0.0008
H ⁺ -PyAsF ₂ ⋯PH ₃	0.0193(0.0114)	0.0281	-0.0012
H ⁺ -PyAsF ₂ ⋯H ₂ O	0.0243(0.0121)	0.0750	0.0005
H ⁺ -PyAsF ₂ ⋯NH ₃	0.0470(0.0299)	0.0683	-0.0104
H ⁺ -PyAsF ₂ ⋯H ₂ CO	0.0269(0.0131)	0.0751	-0.0004

Note: Data in parentheses are the difference of electron density at the intermolecular BCP between the protonated complexes and the neutral analogues.

Table S6 Interaction energies (ΔE , kJ/mol) of pnicogen bonds in the complexes of PyPH₃⁺

	ΔE
PyPH ₃ ⁺ ⋯H ₂ S	-34.0
PyPH ₃ ⁺ ⋯PH ₃	-37.2
PyPH ₃ ⁺ ⋯H ₂ O	-54.9
PyPH ₃ ⁺ ⋯NH ₃	-65.5
PyPH ₃ ⁺ ⋯H ₂ CO	-59.7

Table S7 Electrostatic (ES), exchange (EX), repulsion (REP), polarization (POL), and dispersion (DISP) contributions to interaction energy in the complexes. All are in kJ/mol

System	ES	EX	REP	POL	DISP
H ₂ O⋯PyPH ₂	-49.9	-63.4	114.0	-18.2	-11.4
H ₂ O⋯PyPF ₂	-44.8	-57.7	103.7	-15.8	-12.5
H ₂ O⋯PyAsH ₂	-50.2	-63.5	114.3	-18.5	-11.6
H ₂ O⋯PyAsF ₂	-45.0	-57.9	104.0	-15.8	-12.5
NH ₃ ⋯H ⁺ -PyPH ₂	-122.7	-128.4	247.6	-67.3	-19.7
NH ₃ ⋯H ⁺ -PyPF ₂	-131.8	-138.3	268.2	-76.4	-20.2
NH ₃ ⋯H ⁺ -PyAsH ₂	-123.0	-128.9	248.6	-67.5	-20.0
NH ₃ ⋯H ⁺ -PyAsF ₂	-131.2	-137.8	267.2	-75.7	-20.2

Table S8 Electron densities (ρ , au) at the intermolecular BCPs of hydrogen bonding (HB) and pnictogen bonding (ZB) in the trimers as well as their differences ($\Delta\rho$, au) compared to the corresponding dimers

	ρ_{HB}	ρ_{ZB}	$\Delta\rho_{\text{HB}}$	$\Delta\rho_{\text{ZB}}$
H ₂ O⋯PyPH ₂ ⋯H ₂ O	0.0313	0.0082	0.0008	0.0002
H ₂ O⋯PyPF ₂ ⋯H ₂ O	0.0287	0.0097	0.0006	0.0011
H ₂ O⋯PyAsH ₂ ⋯H ₂ O	0.0316	0.0089	0.0012	0.0005
H ₂ O⋯PyAsF ₂ ⋯H ₂ O	0.0286	0.0131	0.0004	0.0009
NH ₃ ⋯H ⁺ -PyPH ₂ ⋯NH ₃	0.0534	0.0169	-0.0032	-0.0021
NH ₃ ⋯H ⁺ -PyPF ₂ ⋯NH ₃	0.0561	0.0326	-0.0050	-0.0067
NH ₃ ⋯H ⁺ -PyAsH ₂ ⋯NH ₃	0.0533	0.0191	-0.0035	-0.0023
NH ₃ ⋯H ⁺ -PyAsF ₂ ⋯NH ₃	0.0550	0.0550	-0.0058	-0.0055

Table S9 The most positive MEP on the σ -hole of pnicogen atom ($V_{\max,\sigma\text{-hole}}$, kJ/mol) and on the positively charged proton ($V_{\max,\text{H}}$, kJ/mol), the most negative MEP on the nitrogen atom ($V_{\min,\text{N}}$, kJ/mol) in the dimers, and their differences (ΔV , kJ/mol) compared to the isolated molecules

	$V_{\max,\sigma\text{-hole}}$	$\Delta V_{\max,\sigma\text{-hole}}$		$V_{\min,\text{N}}$	$\Delta V_{\min,\text{N}}$
$\text{H}_2\text{O}\cdots\text{PyPH}_2$	106.7	14.6	$\text{PyPH}_2\cdots\text{H}_2\text{O}$	-164.1	-9.2
$\text{H}_2\text{O}\cdots\text{PyPF}_2$	112.9	9.7	$\text{PyPF}_2\cdots\text{H}_2\text{O}$	-135.3	-3.8
$\text{H}_2\text{O}\cdots\text{PyAsH}_2$	108.4	12.8	$\text{PyAsH}_2\cdots\text{H}_2\text{O}$	-165.8	-11.9
$\text{H}_2\text{O}\cdots\text{PyAsF}_2$	125.4	4.4	$\text{PyAsF}_2\cdots\text{H}_2\text{O}$	-135.2	-2.8
	$V_{\max,\sigma\text{-hole}}$	$\Delta V_{\max,\sigma\text{-hole}}$		$V_{\max,\text{H}}$	$\Delta V_{\min,\text{H}}$
$\text{NH}_3\cdots\text{H}^+\text{-PyPH}_2$	377.8	-34.6	$\text{H}^+\text{-PyPH}_2\cdots\text{NH}_3$	604.4	-25.3
$\text{NH}_3\cdots\text{H}^+\text{-PyPF}_2$	392.1	-36.7	$\text{H}^+\text{-PyPF}_2\cdots\text{NH}_3$	617.9	-37.9
$\text{NH}_3\cdots\text{H}^+\text{-PyAsH}_2$	380.7	-34.2	$\text{H}^+\text{-PyAsH}_2\cdots\text{NH}_3$	600.6	-27.6
$\text{NH}_3\cdots\text{H}^+\text{-PyAsF}_2$	407.1	-38.5	$\text{H}^+\text{-PyAsF}_2\cdots\text{NH}_3$	606.4	-44.1

Table S10 Electrostatic (ES), polarization (POL), and dispersion (DISP) contributions to the interaction energy of hydrogen bond in the trimers. All are in kJ/mol

	ES	POL	DISP
$\text{H}_2\text{O}\cdots\text{PyPH}_2\cdots\text{H}_2\text{O}$	-51.7(3.6%)	-19.1(4.9%)	-11.2(-1.8%)
$\text{H}_2\text{O}\cdots\text{PyPF}_2\cdots\text{H}_2\text{O}$	-45.6(1.8%)	-16.3(3.2%)	-12.4(-0.8%)
$\text{H}_2\text{O}\cdots\text{PyAsH}_2\cdots\text{H}_2\text{O}$	-52.3(3.8%)	-19.4(5.2%)	-11.2(-2.1%)
$\text{H}_2\text{O}\cdots\text{PyAsF}_2\cdots\text{H}_2\text{O}$	-45.6(1.3%)	-16.2(2.5%)	-12.4(-0.8%)
$\text{NH}_3\cdots\text{H}^+\text{-PyPH}_2\cdots\text{NH}_3$	-116.4(-5.1%)	-61.2(-9.1%)	-19.1(-3.0%)
$\text{NH}_3\cdots\text{H}^+\text{-PyPF}_2\cdots\text{NH}_3$	-122.1(-7.4%)	-66.4(-13.1%)	-19.4(-4.0%)
$\text{NH}_3\cdots\text{H}^+\text{-PyAsH}_2\cdots\text{NH}_3$	-116.0(-5.7%)	-60.8(-9.9%)	-19.3(-3.5%)
$\text{NH}_3\cdots\text{H}^+\text{-PyAsF}_2\cdots\text{NH}_3$	-119.7(-8.8%)	-64.2(-15.2%)	-19.3(-4.5%)

Note: Data in parentheses are the increased/decreased percentage of each energy term in the trimer relative to the corresponding dimer.

Table S11 Electrostatic (ES), polarization (POL), and dispersion (DISP) contributions to the interaction energy of pnictogen bond in the trimers. All are in kJ/mol

	ES	POL	DISP
H ₂ O⋯PyPH ₂ ⋯H ₂ O	-14.8(5.7%)	-3.4(9.7%)	-5.9(-3.3%)
H ₂ O⋯PyPF ₂ ⋯H ₂ O	-20.6(6.7%)	-4.7(20.5%)	-5.9(1.7%)
H ₂ O⋯PyAsH ₂ ⋯H ₂ O	-16.4(13.9%)	-4.3(19.4%)	-6.0(-1.6%)
H ₂ O⋯PyAsF ₂ ⋯H ₂ O	-37.8(4.4%)	-8.7(10.1%)	-7.7(1.3%)
NH ₃ ⋯H ⁺ -PyPH ₂ ⋯NH ₃	-54.0(-13.9%)	-18.6(-19.1%)	-11.3(-9.6%)
NH ₃ ⋯H ⁺ -PyPF ₂ ⋯NH ₃	-109.4(-20.0%)	-49.4(-27.1%)	-16.3(-11.4%)
NH ₃ ⋯H ⁺ -PyAsH ₂ ⋯NH ₃	-65.1(-13.5%)	-22.9(-18.2%)	-12.0(-7.7%)
NH ₃ ⋯H ⁺ -PyAsF ₂ ⋯NH ₃	-159.9(-14.5%)	-76.5(-19.9%)	-17.0(1.2%)

Note: Data in parentheses are the increased/decreased percentage of each energy term in the trimer relative to the corresponding dimer.