Functional formamidines: pyridine substituents make an exception in the usual doubly hydrogen-bonded formamidine dimer

Anne Petitjean*, Liyan Xing, Ruiyao Wang

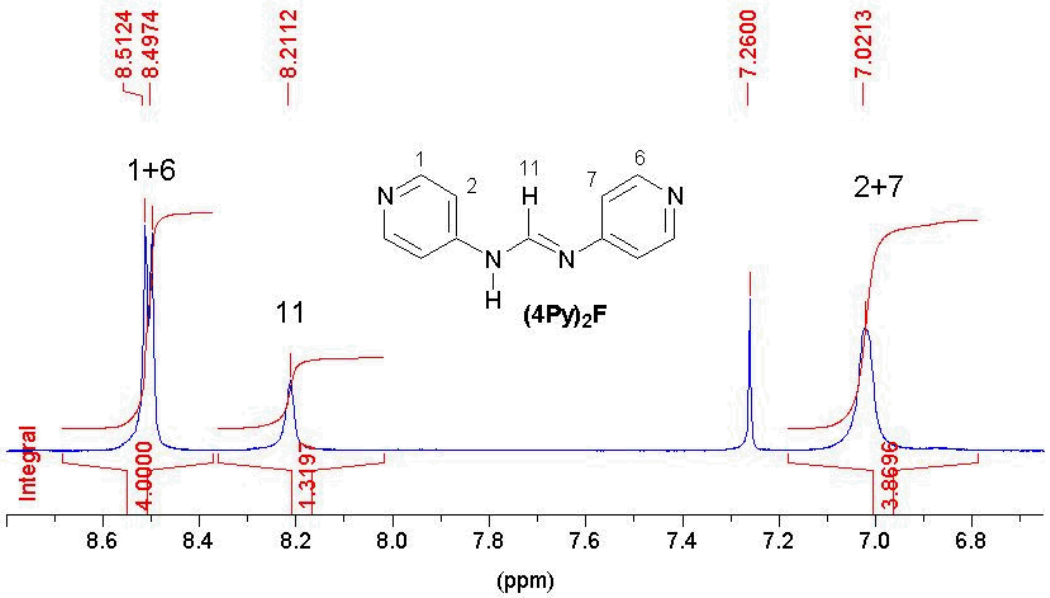
Supplementary Information:

Content:

$(4Py)_2F$

$(2Py)_2F$

a



b

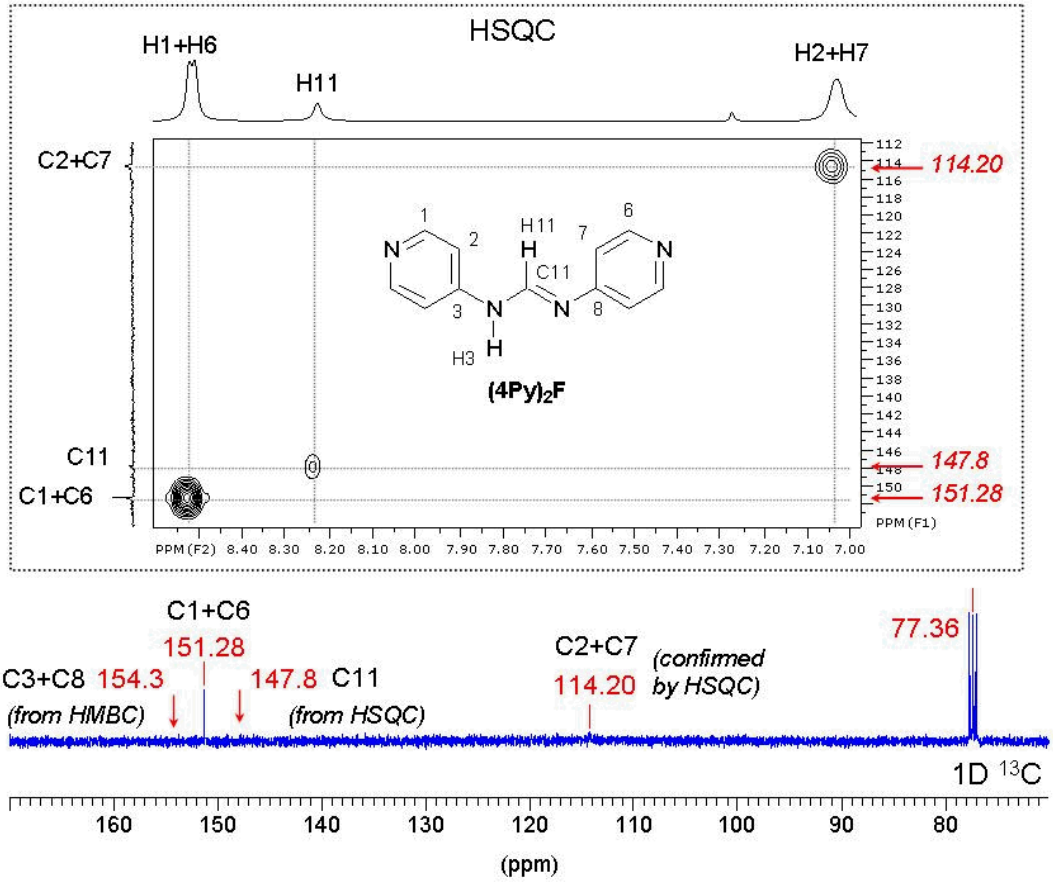


Fig S1. a) ^{1}H NMR spectrum for **(4Py)$_2$F** ($CDCl_3$, 400 MHz, 25°C), b) ^{13}C NMR spectrum for **(4Py)$_2$F**, with 2D HMBC analysis in insert ($CDCl_3$, 100 MHz, 25°C).

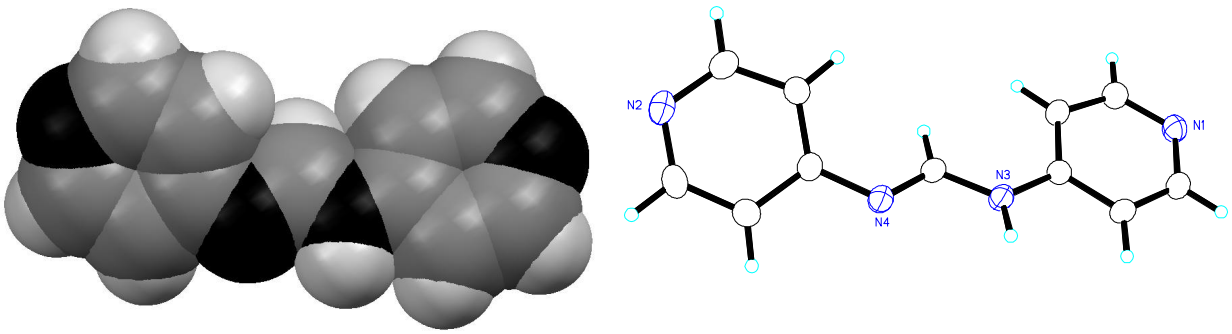


Fig. S2: Front view of **$(4Py)_2F$** in the solid state (CPK left; Ortep right).

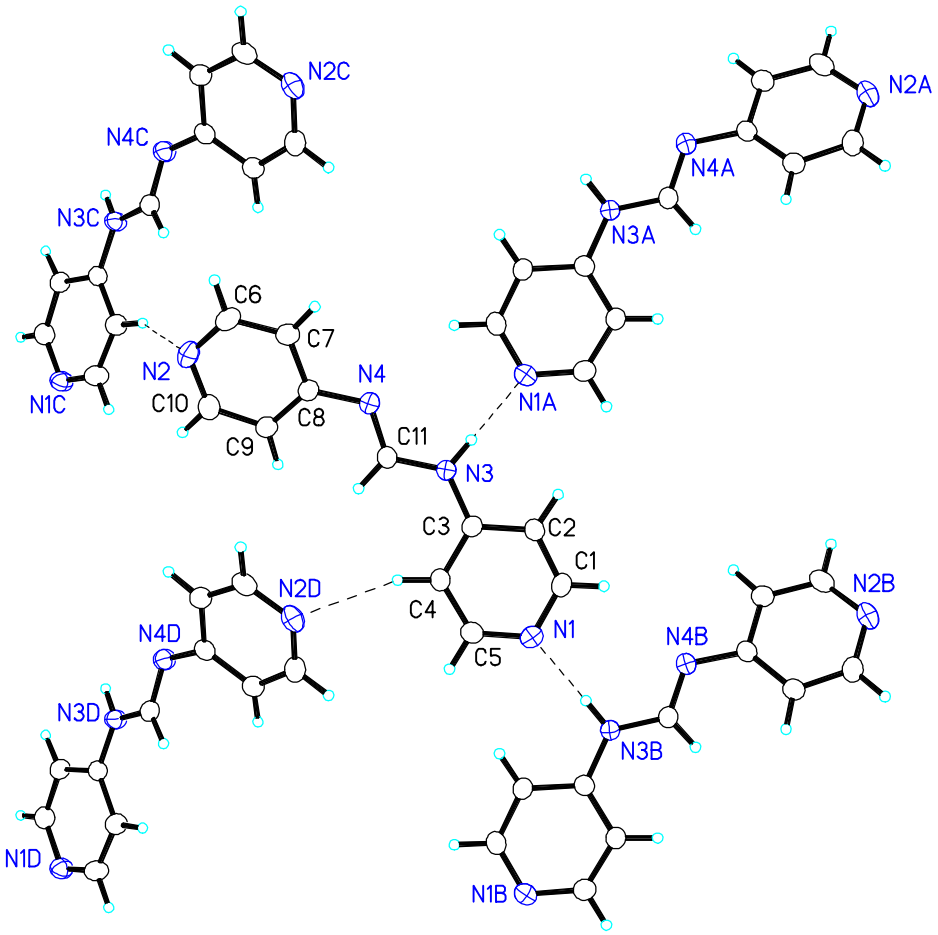


Fig. S3: Hydrogen bonded network for **$(4Py)_2F$** in the solid state.

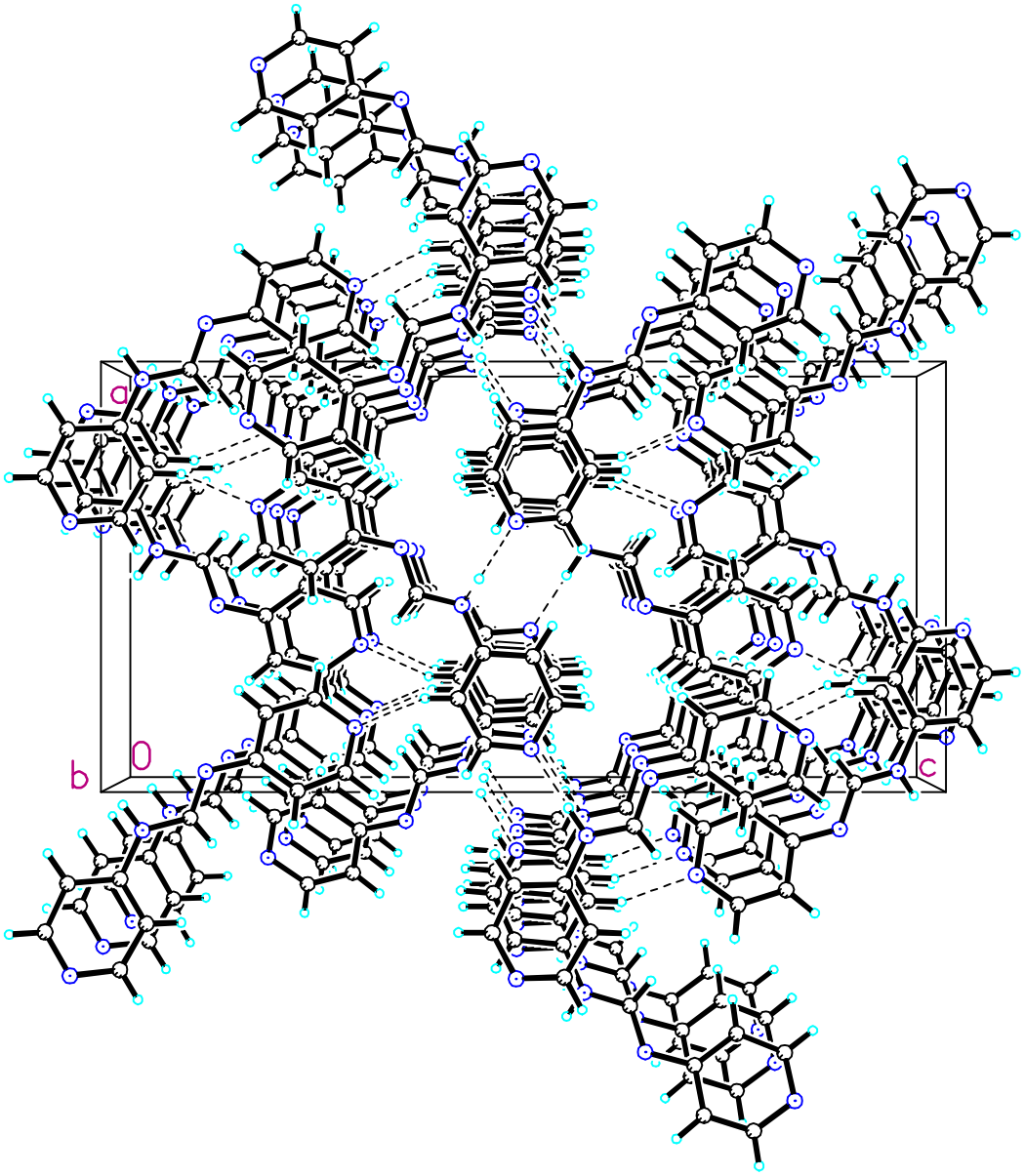


Fig. S4: Unit cell packing in **$(2Py)_2F$** crystal structure.

Table S1. Crystal data and structure refinement for ap11

Identification code	ap11	
Empirical formula	C11 H10 N4	
Formula weight	198.23	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.7861(5) Å	α= 90°.
	b = 7.2290(3) Å	β= 90°.
	c = 23.2069(9) Å	γ = 90°.
Volume	1977.27(14) $Å^3$	
Z	8	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	832	
Crystal size	0.25 x 0.25 x 0.20 mm^3	
Theta range for data collection	2.46 to 25.99°.	
Index ranges	-14<=h<=11, -8<=k<=8, -28<=l<=28	
Reflections collected	6973	
Independent reflections	1938 [R(int) = 0.0156]	
Completeness to theta = 25.99°	99.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9831 and 0.9790	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1938 / 0 / 141	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0855	
R indices (all data)	R1 = 0.0357, wR2 = 0.0893	
Extinction coefficient	0.0100(12)	
Largest diff. peak and hole	0.183 and -0.147 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ap11. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3784(1)	2024(1)	5082(1)	29(1)
N(2)	-1591(1)	-1465(1)	1946(1)	30(1)
N(3)	618(1)	1176(1)	4302(1)	26(1)
N(4)	-657(1)	348(1)	3609(1)	28(1)
C(1)	2799(1)	2371(2)	5349(1)	28(1)
C(2)	1752(1)	2058(2)	5107(1)	26(1)
C(3)	1686(1)	1383(2)	4544(1)	23(1)
C(4)	2702(1)	989(2)	4262(1)	26(1)
C(5)	3703(1)	1319(2)	4549(1)	30(1)
C(6)	-2234(1)	-1740(2)	2413(1)	29(1)
C(7)	-1937(1)	-1201(2)	2964(1)	28(1)
C(8)	-900(1)	-317(2)	3057(1)	24(1)
C(9)	-213(1)	-42(2)	2572(1)	25(1)
C(10)	-595(1)	-631(2)	2040(1)	29(1)
C(11)	374(1)	411(2)	3784(1)	24(1)

Table S3: Bond lengths [Å] and angles [°] for ap11.

N(1)-C(1)	1.3390(14)	N(1)-C(1)-H(1A)	118.0
N(1)-C(5)	1.3422(14)	C(2)-C(1)-H(1A)	118.0
N(2)-C(10)	1.3374(15)	C(1)-C(2)-C(3)	119.24(10)
N(2)-C(6)	1.3383(15)	C(1)-C(2)-H(2A)	120.4
N(3)-C(11)	1.3544(13)	C(3)-C(2)-H(2A)	120.4
N(3)-C(3)	1.3867(13)	N(3)-C(3)-C(4)	124.57(9)
N(3)-H(3N)	0.900(14)	N(3)-C(3)-C(2)	117.86(9)
N(4)-C(11)	1.2824(14)	C(4)-C(3)-C(2)	117.56(10)
N(4)-C(8)	1.3983(13)	C(5)-C(4)-C(3)	118.33(10)
C(1)-C(2)	1.3734(15)	C(5)-C(4)-H(4A)	120.8
C(1)-H(1A)	0.9500	C(3)-C(4)-H(4A)	120.8
C(2)-C(3)	1.3972(14)	N(1)-C(5)-C(4)	124.97(10)
C(2)-H(2A)	0.9500	N(1)-C(5)-H(5A)	117.5
C(3)-C(4)	1.3932(15)	C(4)-C(5)-H(5A)	117.5
C(4)-C(5)	1.3753(15)	N(2)-C(6)-C(7)	124.37(10)
C(4)-H(4A)	0.9500	N(2)-C(6)-H(6A)	117.8
C(5)-H(5A)	0.9500	C(7)-C(6)-H(6A)	117.8
C(6)-C(7)	1.3811(15)	C(6)-C(7)-C(8)	119.59(10)
C(6)-H(6A)	0.9500	C(6)-C(7)-H(7A)	120.2
C(7)-C(8)	1.3958(15)	C(8)-C(7)-H(7A)	120.2
C(7)-H(7A)	0.9500	C(7)-C(8)-N(4)	118.57(10)
C(8)-C(9)	1.4006(15)	C(7)-C(8)-C(9)	116.57(9)
C(9)-C(10)	1.3817(15)	N(4)-C(8)-C(9)	124.67(10)
C(9)-H(9A)	0.9500	C(10)-C(9)-C(8)	119.07(10)
C(10)-H(10A)	0.9500	C(10)-C(9)-H(9A)	120.5
C(11)-H(11A)	0.9500	C(8)-C(9)-H(9A)	120.5
		N(2)-C(10)-C(9)	124.79(10)
C(1)-N(1)-C(5)	115.75(9)	N(2)-C(10)-H(10A)	117.6
C(10)-N(2)-C(6)	115.59(9)	C(9)-C(10)-H(10A)	117.6
C(11)-N(3)-C(3)	126.65(9)	N(4)-C(11)-N(3)	119.79(10)
C(11)-N(3)-H(3N)	117.2(9)	N(4)-C(11)-H(11A)	120.1
C(3)-N(3)-H(3N)	116.0(9)	N(3)-C(11)-H(11A)	120.1
C(11)-N(4)-C(8)	119.76(9)		
N(1)-C(1)-C(2)	124.08(10)		

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ap11.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	24(1)	35(1)	29(1)	-3(1)	-3(1)	-2(1)
N(2)	36(1)	29(1)	26(1)	-1(1)	-8(1)	1(1)
N(3)	21(1)	36(1)	21(1)	-4(1)	0(1)	1(1)
N(4)	24(1)	38(1)	22(1)	-4(1)	-1(1)	-1(1)
C(1)	29(1)	32(1)	21(1)	-2(1)	-2(1)	-2(1)
C(2)	25(1)	31(1)	21(1)	-1(1)	2(1)	0(1)
C(3)	23(1)	24(1)	21(1)	1(1)	-1(1)	0(1)
C(4)	26(1)	30(1)	23(1)	-4(1)	1(1)	0(1)
C(5)	24(1)	34(1)	31(1)	-5(1)	1(1)	1(1)
C(6)	27(1)	26(1)	34(1)	0(1)	-9(1)	-1(1)
C(7)	24(1)	32(1)	27(1)	2(1)	-1(1)	-1(1)
C(8)	23(1)	25(1)	22(1)	0(1)	-3(1)	3(1)
C(9)	23(1)	25(1)	26(1)	0(1)	-2(1)	0(1)
C(10)	35(1)	29(1)	23(1)	1(1)	0(1)	1(1)
C(11)	25(1)	27(1)	20(1)	0(1)	1(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ap11.

	x	y	z	U(eq)
H(3N)	38(12)	1670(20)	4502(5)	37(4)
H(1A)	2825	2863	5728	33
H(2A)	1080	2297	5321	31
H(4A)	2703	505	3882	32
H(5A)	4389	1024	4355	35
H(6A)	-2942	-2346	2363	35
H(7A)	-2436	-1430	3278	33
H(9A)	505	542	2608	30
H(10A)	-115	-428	1717	35
H(11A)	965	-78	3551	28

Table S6. Hydrogen bonds for ap11 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...N(1)#1	0.900(14)	2.001(15)	2.8996(13)	175.2(13)
C(4)-H(4A)...N(2)#2	0.95	2.53	3.4212(14)	155.9

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,-z+1 #2 x+1/2,y,-z+1/2

Table S7. Torsion angles [°] for ap11.

C(5)-N(1)-C(1)-C(2)	-0.39(17)
N(1)-C(1)-C(2)-C(3)	-1.80(18)
C(11)-N(3)-C(3)-C(4)	6.61(18)
C(11)-N(3)-C(3)-C(2)	-174.32(10)
C(1)-C(2)-C(3)-N(3)	-176.59(10)
C(1)-C(2)-C(3)-C(4)	2.54(16)
N(3)-C(3)-C(4)-C(5)	177.86(11)
C(2)-C(3)-C(4)-C(5)	-1.21(16)
C(1)-N(1)-C(5)-C(4)	1.88(18)
C(3)-C(4)-C(5)-N(1)	-1.07(18)
C(10)-N(2)-C(6)-C(7)	0.95(17)
N(2)-C(6)-C(7)-C(8)	-0.46(18)
C(6)-C(7)-C(8)-N(4)	174.94(10)
C(6)-C(7)-C(8)-C(9)	-0.33(16)
C(11)-N(4)-C(8)-C(7)	149.62(11)
C(11)-N(4)-C(8)-C(9)	-35.52(16)
C(7)-C(8)-C(9)-C(10)	0.56(15)
N(4)-C(8)-C(9)-C(10)	-174.39(10)
C(6)-N(2)-C(10)-C(9)	-0.69(17)
C(8)-C(9)-C(10)-N(2)	-0.05(17)
C(8)-N(4)-C(11)-N(3)	175.33(10)
C(3)-N(3)-C(11)-N(4)	-178.47(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,-z+1 #2 x+1/2,y,-z+1/2

$(2Py)_2F$

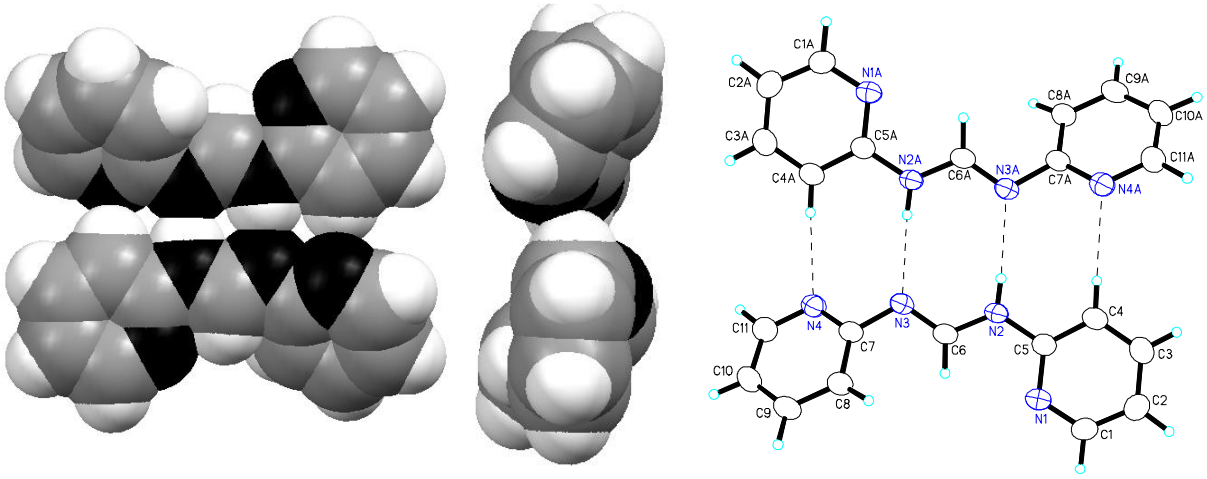


Fig. S5: Front (left) and side (middle) views of the **$(2Py)_2F$** in the solid state (CPK representation). Note the twist in the side view. Ortep representation of the **$(2Py)_2F$** dimer (right).

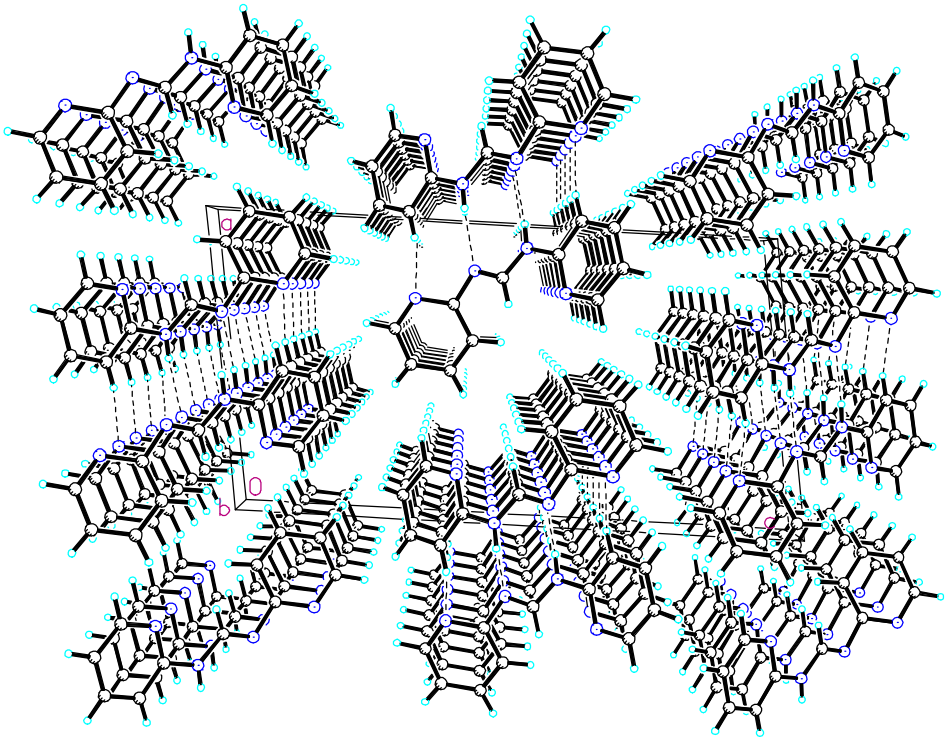


Fig. S6: Unit cell packing in **$(2Py)_2F$** crystal structure.

Table S8. Crystal data and structure refinement for ap04t

Identification code	ap04t	
Empirical formula	C11 H10 N4	
Formula weight	198.23	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 10.9881(19) Å	α= 90°.
	b = 4.3351(7) Å	β= 98.561(3)°.
	c = 20.561(4) Å	γ = 90°.
Volume	968.5(3) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	416	
Crystal size	0.35 x 0.25 x 0.15 mm^3	
Theta range for data collection	1.99 to 25.99°.	
Index ranges	-11<=h<=13, -5<=k<=5, -25<=l<=25	
Reflections collected	5802	
Independent reflections	1911 [R(int) = 0.0399]	
Completeness to theta = 25.99°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9870 and 0.9701	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1911 / 0 / 176	
Goodness-of-fit on F^2	0.973	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0843	
R indices (all data)	R1 = 0.0436, wR2 = 0.0893	
Largest diff. peak and hole	0.143 and -0.168 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ap04t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2182(1)	-867(2)	3993(1)	34(1)
N(2)	884(1)	2169(2)	4529(1)	32(1)
N(3)	1656(1)	5298(2)	5402(1)	32(1)
N(4)	2605(1)	7000(2)	6422(1)	39(1)
C(1)	2309(1)	-2904(3)	3516(1)	37(1)
C(2)	1349(1)	-4103(3)	3088(1)	39(1)
C(3)	165(1)	-3168(3)	3156(1)	39(1)
C(4)	2(1)	-1087(3)	3637(1)	35(1)
C(5)	1035(1)	17(2)	4043(1)	30(1)
C(6)	1820(1)	3301(2)	4962(1)	31(1)
C(7)	2727(1)	6418(2)	5796(1)	32(1)
C(8)	3815(1)	7037(3)	5542(1)	36(1)
C(9)	4806(1)	8221(3)	5957(1)	41(1)
C(10)	4694(1)	8790(3)	6604(1)	43(1)
C(11)	3586(1)	8164(3)	6810(1)	43(1)

Table S10. Bond lengths [Å] and angles [°] for ap04t

N(1)-C(5)	1.3365(14)	C(5)-N(1)-C(1)	116.60(10)
N(1)-C(1)	1.3408(16)	C(6)-N(2)-C(5)	123.72(10)
N(2)-C(6)	1.3476(15)	C(6)-N(2)-H(2N)	119.8(9)
N(2)-C(5)	1.3950(15)	C(5)-N(2)-H(2N)	116.3(9)
N(2)-H(2N)	0.850(14)	C(6)-N(3)-C(7)	116.31(10)
N(3)-C(6)	1.2847(15)	C(7)-N(4)-C(11)	117.22(11)
N(3)-C(7)	1.4119(14)	N(1)-C(1)-C(2)	124.35(12)
N(4)-C(7)	1.3383(15)	N(1)-C(1)-H(1)	116.7(7)
N(4)-C(11)	1.3409(16)	C(2)-C(1)-H(1)	119.0(7)
C(1)-C(2)	1.3720(18)	C(1)-C(2)-C(3)	117.85(12)
C(1)-H(1)	0.976(14)	C(1)-C(2)-H(2)	120.4(7)
C(2)-C(3)	1.3888(18)	C(3)-C(2)-H(2)	121.8(7)
C(2)-H(2)	0.984(13)	C(4)-C(3)-C(2)	119.38(12)
C(3)-C(4)	1.3697(17)	C(4)-C(3)-H(3)	118.0(8)

C(3)-H(3)	0.952(14)	C(2)-C(3)-H(3)	122.6(8)
C(4)-C(5)	1.3907(16)	C(3)-C(4)-C(5)	118.47(11)
C(4)-H(4)	0.919(13)	C(3)-C(4)-H(4)	122.1(8)
C(6)-H(6)	0.964(11)	C(5)-C(4)-H(4)	119.4(8)
C(7)-C(8)	1.3992(16)	N(1)-C(5)-C(4)	123.35(11)
C(8)-C(9)	1.3787(17)	N(1)-C(5)-N(2)	117.53(10)
C(8)-H(8)	0.956(12)	C(4)-C(5)-N(2)	119.11(10)
C(9)-C(10)	1.3757(18)	N(3)-C(6)-N(2)	122.45(11)
C(9)-H(9)	0.959(13)	N(3)-C(6)-H(6)	124.3(6)
C(10)-C(11)	1.3744(18)	N(2)-C(6)-H(6)	113.2(6)
C(10)-H(10)	0.945(14)	N(4)-C(7)-C(8)	122.37(11)
C(11)-H(11)	0.998(13)	N(4)-C(7)-N(3)	114.99(10)
		C(8)-C(7)-N(3)	122.56(11)
Symmetry transformations used to generate equivalent atoms.		C(9)-C(8)-C(7)	118.77(12)
		C(9)-C(8)-H(8)	122.3(7)
		C(7)-C(8)-H(8)	118.8(7)
		C(10)-C(9)-C(8)	119.23(12)
		C(10)-C(9)-H(9)	121.7(8)
		C(8)-C(9)-H(9)	119.0(8)
		C(11)-C(10)-C(9)	118.31(12)
		C(11)-C(10)-H(10)	119.8(8)
		C(9)-C(10)-H(10)	121.9(8)
		N(4)-C(11)-C(10)	124.09(12)
		N(4)-C(11)-H(11)	115.2(8)
		C(10)-C(11)-H(11)	120.8(8)

Table S11. Torsion angles [°] for ap04t.

C(5)-N(1)-C(1)-C(2)	0.01(17)
N(1)-C(1)-C(2)-C(3)	-0.60(18)
C(1)-C(2)-C(3)-C(4)	0.64(17)
C(2)-C(3)-C(4)-C(5)	-0.12(17)
C(1)-N(1)-C(5)-C(4)	0.57(16)
C(1)-N(1)-C(5)-N(2)	-179.08(10)
C(3)-C(4)-C(5)-N(1)	-0.51(17)
C(3)-C(4)-C(5)-N(2)	179.13(10)
C(6)-N(2)-C(5)-N(1)	-2.64(16)

C(6)-N(2)-C(5)-C(4)	177.70(10)
C(7)-N(3)-C(6)-N(2)	-176.32(10)
C(5)-N(2)-C(6)-N(3)	179.54(10)
C(11)-N(4)-C(7)-C(8)	-1.27(17)
C(11)-N(4)-C(7)-N(3)	-177.86(10)
C(6)-N(3)-C(7)-N(4)	-144.63(10)
C(6)-N(3)-C(7)-C(8)	38.79(15)
N(4)-C(7)-C(8)-C(9)	1.60(18)
N(3)-C(7)-C(8)-C(9)	177.93(11)
C(7)-C(8)-C(9)-C(10)	-0.74(19)
C(8)-C(9)-C(10)-C(11)	-0.3(2)
C(7)-N(4)-C(11)-C(10)	0.11(19)
C(9)-C(10)-C(11)-N(4)	0.7(2)

Symmetry transformations used to generate equivalent atoms:

Table S12. Hydrogen bonds for ap04t [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...N(3)#1	0.850(14)	2.173(15)	3.0212(14)	175.6(12)
C(4)-H(4)...N(4)#1	0.919(13)	2.475(14)	3.3545(16)	160.2(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1