Unprecedented Conformational Variability in Main Group Inorganic Chemistry: the Tetraazidoarsenite and -Antimonite Salts $A^+[M(N_3)_4]^-$ (A = NMe_4, PPh_4, $(Ph_3P)_2N$; M = As, Sb), Five Similar Salts, Five Different Anion Structures

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Supporting Information

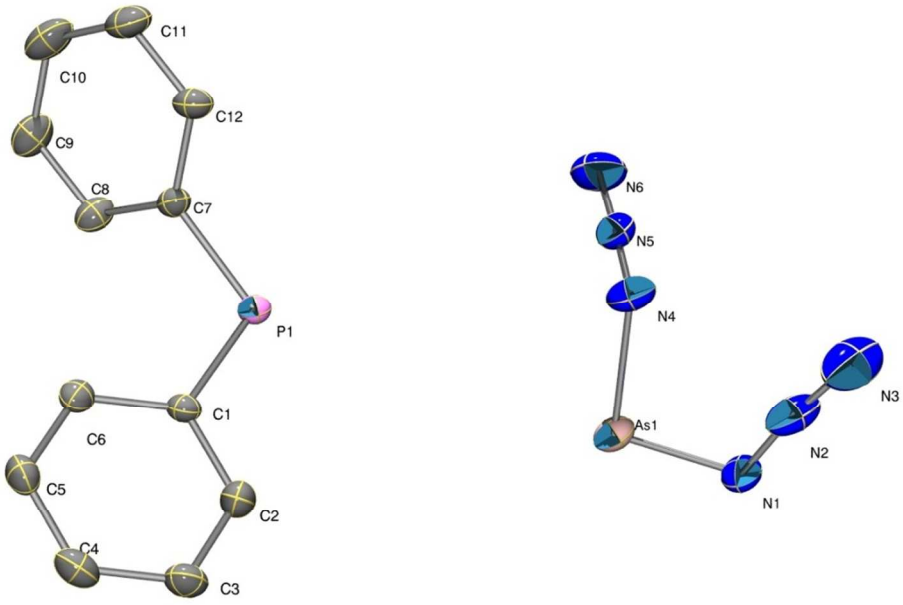

Figure S1: Asymmetric unit in the crystal structure of $[PPh_4][As(N_3)_4]$. Thermal ellipsoids are shown at the 30% probability level.

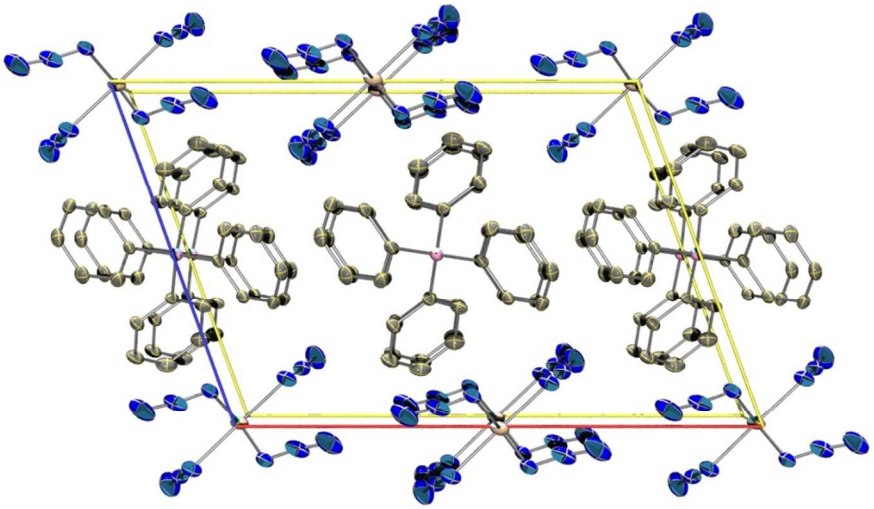

Figure S2: Unit cell of $[PPh_4][As(N_3)_4]$. View normal to (010). Thermal ellipsoids are shown at the 30% probability level.

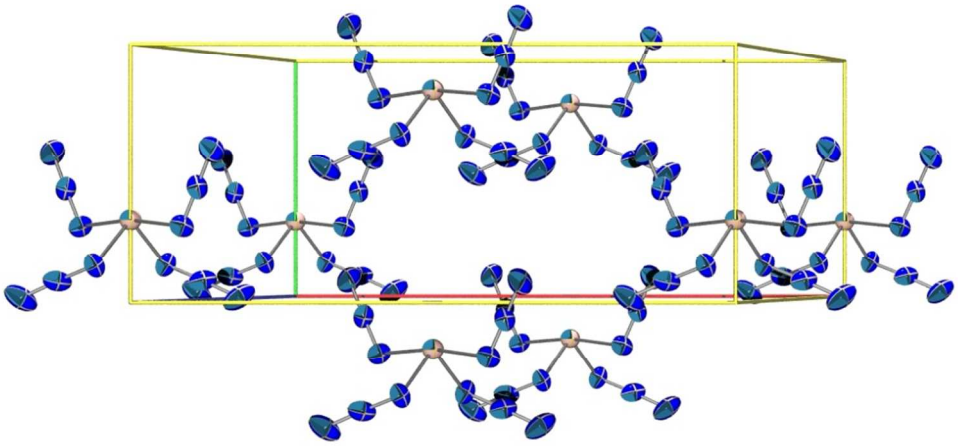

Figure S3: Unit cell of $[PPh_4][As(N_3)_4]$. View normal to (001), the PPh_4^+ cations have been omitted. Thermal ellipsoids are shown at the 30% probability level.

Table S1. Crystal data and structure refinement for $[PPh_4][As(N_3)_4]$.

Empirical formula	C24 H20 As N12 P	
Formula weight	582.41	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 16.723(5) Å	α= 90°.
	b = 7.161(2) Å	β= 109.853(4)°.
	c = 11.702(3) Å	γ = 90°.
Volume	1318.0(6) $Å^3$	
Z	2	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	1.389 mm^{-1}	
F(000)	592	
Crystal size	0.15 x 0.09 x 0.05 mm^3	
Theta range for data collection	1.85 to 27.45°.	
Index ranges	-20<=h<=21, -9<=k<=9, -14<=l<=10	
Reflections collected	4625	
Independent reflections	2846 [R(int) = 0.0310]	
Completeness to theta = 27.00°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Transmission factors	min/max: 0.912	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2846 / 1 / 173	
Goodness-of-fit on F^2	0.946	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.0816	
R indices (all data)	R1 = 0.0667, wR2 = 0.0890	
Absolute structure parameter	0.012(12)	
Largest diff. peak and hole	0.434 and -0.229 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4][As(N_3)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
As(1)	5000	8201(1)	0	49(1)
C(1)	4200(2)	5612(5)	5190(3)	31(1)
C(2)	3822(2)	4293(6)	4292(4)	43(1)
C(3)	3226(2)	3061(7)	4424(4)	45(1)
C(4)	3016(2)	3109(7)	5469(4)	45(1)
C(5)	3393(2)	4385(6)	6371(4)	40(1)
C(6)	3978(2)	5654(5)	6231(3)	35(1)
C(7)	5438(2)	8578(5)	6297(3)	32(1)
C(8)	4938(3)	9955(5)	6548(3)	40(1)
C(9)	5261(3)	11056(6)	7567(4)	51(1)
C(10)	6102(3)	10850(6)	8317(4)	58(1)
C(11)	6608(3)	9530(7)	8064(4)	53(1)
C(12)	6291(2)	8403(7)	7054(3)	41(1)
N(1)	5286(2)	6457(6)	-1008(3)	58(1)
N(2)	6000(3)	5843(6)	-672(4)	70(1)
N(3)	6662(3)	5186(7)	-475(5)	104(2)
N(4)	6235(2)	7960(7)	1329(3)	61(1)
N(5)	6567(2)	9421(7)	1603(3)	57(1)
N(6)	6885(3)	10840(7)	1899(5)	93(2)
P(1)	5000	7107(2)	5000	31(1)

Table S3. Bond lengths [Å] and angles [°] for $[PPh_4][As(N_3)_4]$.

As(1)-N(1)#1	1.888(4)
As(1)-N(1)	1.888(4)
As(1)-N(4)#1	2.129(4)
As(1)-N(4)	2.129(4)
C(1)-C(6)	1.389(5)
C(1)-C(2)	1.395(5)
C(1)-P(1)	1.786(4)
C(2)-C(3)	1.379(5)
C(3)-C(4)	1.381(5)
C(4)-C(5)	1.376(6)
C(5)-C(6)	1.385(5)
C(7)-C(8)	1.386(5)
C(7)-C(12)	1.406(4)
C(7)-P(1)	1.787(4)
C(8)-C(9)	1.377(5)
C(9)-C(10)	1.390(6)
C(10)-C(11)	1.367(6)
C(11)-C(12)	1.380(6)
N(1)-N(2)	1.206(5)
N(2)-N(3)	1.152(5)
N(4)-N(5)	1.177(6)
N(5)-N(6)	1.144(5)
P(1)-C(1)#2	1.786(4)
P(1)-C(7)#2	1.787(4)
N(1)#1-As(1)-N(1)	97.2(2)
N(1)#1-As(1)-N(4)#1	90.82(16)
N(1)-As(1)-N(4)#1	83.03(16)
N(1)#1-As(1)-N(4)	83.03(16)
N(1)-As(1)-N(4)	90.82(16)
N(4)#1-As(1)-N(4)	170.7(3)
C(6)-C(1)-C(2)	119.2(3)
C(6)-C(1)-P(1)	122.0(3)
C(2)-C(1)-P(1)	118.6(3)

C(3)-C(2)-C(1)	120.6(4)
C(2)-C(3)-C(4)	119.6(4)
C(5)-C(4)-C(3)	120.5(4)
C(4)-C(5)-C(6)	120.2(4)
C(5)-C(6)-C(1)	119.9(4)
C(8)-C(7)-C(12)	119.0(3)
C(8)-C(7)-P(1)	119.8(3)
C(12)-C(7)-P(1)	121.2(3)
C(9)-C(8)-C(7)	120.2(4)
C(8)-C(9)-C(10)	120.1(4)
C(11)-C(10)-C(9)	120.3(4)
C(10)-C(11)-C(12)	120.3(4)
C(11)-C(12)-C(7)	120.0(4)
N(2)-N(1)-As(1)	118.0(3)
N(3)-N(2)-N(1)	172.7(5)
N(5)-N(4)-As(1)	112.2(4)
N(6)-N(5)-N(4)	178.0(5)
C(1)-P(1)-C(1)#2	106.3(2)
C(1)-P(1)-C(7)	110.84(16)
C(1)#2-P(1)-C(7)	110.55(16)
C(1)-P(1)-C(7)#2	110.55(15)
C(1)#2-P(1)-C(7)#2	110.84(16)
C(7)-P(1)-C(7)#2	107.8(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4][As(N_3)_4]$. 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}
As(1)	53(1)	55(1)	32(1)	0	3(1)	0
C(1)	24(2)	35(2)	31(2)	0(2)	5(2)	-2(2)
C(2)	41(2)	50(2)	41(3)	-9(2)	17(2)	-4(2)
C(3)	36(2)	42(2)	55(2)	-8(3)	13(2)	-11(2)
C(4)	32(2)	42(2)	61(3)	5(3)	16(2)	-3(2)
C(5)	35(2)	48(2)	40(3)	6(2)	18(2)	3(2)
C(6)	28(2)	41(2)	34(2)	-2(2)	7(2)	6(2)
C(7)	33(2)	34(3)	29(2)	-1(2)	8(2)	-6(2)
C(8)	45(2)	36(2)	32(2)	2(2)	4(2)	6(2)
C(9)	69(3)	37(2)	44(3)	-3(2)	16(2)	2(2)
C(10)	78(3)	44(3)	43(3)	-9(2)	8(3)	-13(3)
C(11)	46(3)	64(3)	38(3)	-6(2)	-2(2)	-9(2)
C(12)	32(2)	47(3)	39(2)	-1(2)	4(2)	-4(2)
N(1)	46(2)	79(3)	39(2)	-9(2)	2(2)	9(2)
N(2)	81(3)	55(3)	52(3)	-7(2)	-7(2)	6(2)
N(3)	93(4)	92(4)	91(4)	-17(3)	-14(3)	41(3)
N(4)	61(2)	64(3)	45(2)	-4(2)	2(2)	-9(2)
N(5)	53(2)	75(3)	41(2)	-9(2)	13(2)	-9(2)
N(6)	69(3)	91(4)	108(4)	-33(3)	16(3)	-27(3)
P(1)	28(1)	36(1)	28(1)	0	6(1)	0

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $[PPh_4][As(N_3)_4]$.

	x	y	z	U(eq)
H(2)	3976	4242	3583	52
H(3)	2960	2185	3801	54
H(4)	2609	2255	5565	54
H(5)	3252	4394	7091	48
H(6)	4228	6553	6847	42
H(8)	4372	10140	6015	48
H(9)	4908	11957	7757	61
H(10)	6326	11630	9010	70
H(11)	7181	9387	8585	64
H(12)	6649	7508	6870	50

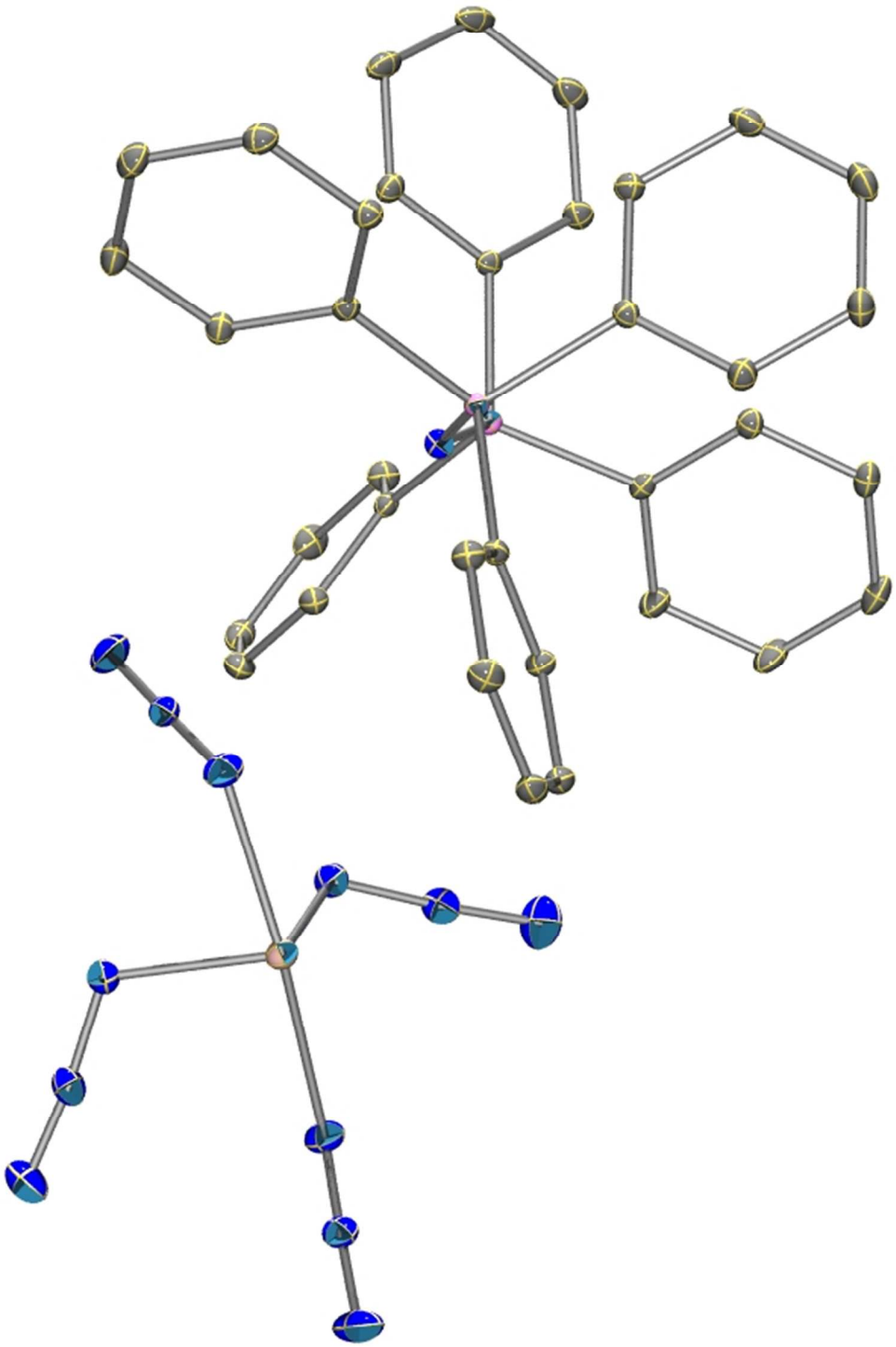

Figure S4: Asymmetric unit in the crystal structure of [PNP][As$(N_3)_4$]. Thermal ellipsoids are shown at the 30% probability level.

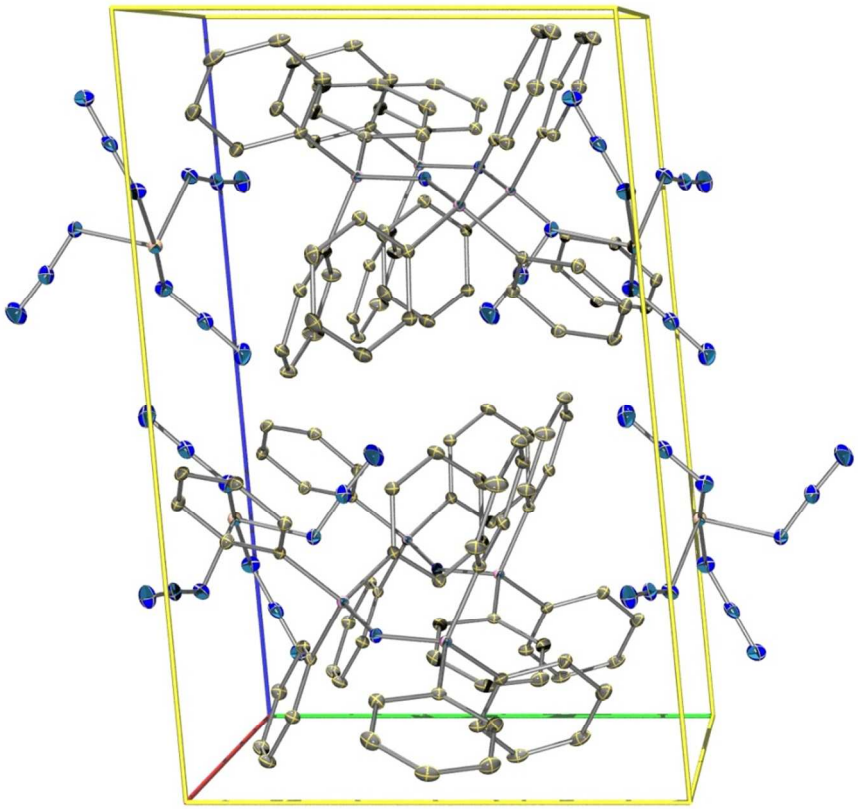

Figure S5: Unit cell of [PNP][As(N_3)$_4$]. View normal to (100). Thermal ellipsoids are shown at the 30% probability level.

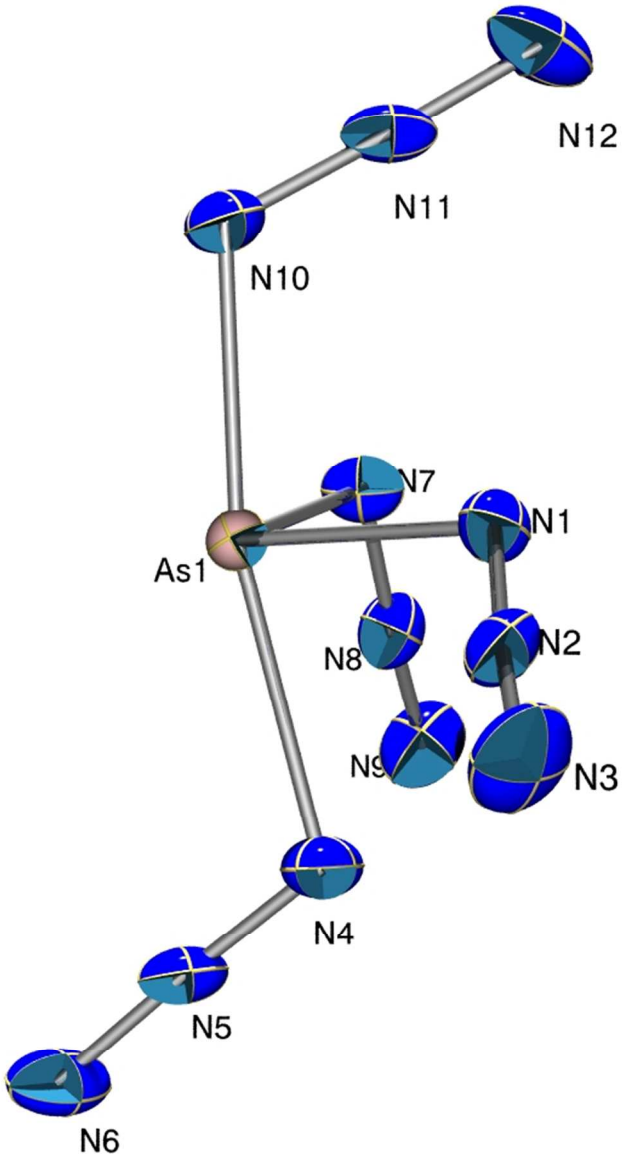

Figure S6: The anion of [PNP][As(N_3)$_4$]. Thermal ellipsoids are shown at the 50% probability level.

Table S6. Crystal data and structure refinement for [PNP][As$(N_3)_4$].

Empirical formula	C36 H30 As N13 P2	
Formula weight	781.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.2141(2) Å	α= 95.3480(10)°.
	b = 10.6072(2) Å	β= 94.1720(10)°.
	c = 16.8394(3) Å	γ = 97.2930(10)°.
Volume	1795.17(6) $Å^3$	
Z	2	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	1.084 mm^{-1}	
F(000)	800	
Crystal size	0.34 x 0.28 x 0.25 mm^3	
Theta range for data collection	1.95 to 30.62°.	
Index ranges	-14<=h<=14, -15<=k<=15, -24<=l<=24	
Reflections collected	68197	
Independent reflections	11030 [R(int) = 0.0383]	
Completeness to theta = 27.5°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7734 and 0.7095	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11030 / 0 / 469	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0642	
R indices (all data)	R1 = 0.0348, wR2 = 0.0674	
Largest diff. peak and hole	0.416 and -0.352 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [PNP][As(N_3)$_4$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
As(1)	3804(1)	341(1)	3106(1)	18(1)
C(1)	-3063(1)	6085(1)	3840(1)	25(1)
C(2)	-2320(1)	5313(1)	4257(1)	24(1)
C(3)	-1637(1)	4442(1)	3844(1)	19(1)
C(4)	-1700(1)	4343(1)	3010(1)	14(1)
C(5)	144(1)	6501(1)	1572(1)	14(1)
C(6)	-590(1)	5854(1)	885(1)	18(1)
C(7)	-1398(1)	6505(1)	415(1)	24(1)
C(8)	-1487(1)	7789(2)	630(1)	26(1)
C(9)	2312(1)	7549(1)	4687(1)	24(1)
C(10)	3286(1)	7132(2)	4238(1)	27(1)
C(11)	2965(1)	6586(1)	3452(1)	22(1)
C(12)	1656(1)	6465(1)	3113(1)	15(1)
C(13)	-3143(1)	5977(1)	3008(1)	23(1)
C(14)	-2470(1)	5108(1)	2591(1)	18(1)
C(15)	-76(1)	2310(1)	3139(1)	14(1)
C(16)	-831(1)	1141(1)	3218(1)	18(1)
C(17)	-362(1)	332(1)	3746(1)	20(1)
C(18)	843(1)	698(1)	4200(1)	18(1)
C(19)	1582(1)	1870(1)	4132(1)	18(1)
C(20)	1133(1)	2676(1)	3597(1)	16(1)
C(21)	-1643(1)	2462(1)	1640(1)	14(1)
C(22)	-1010(1)	2094(1)	962(1)	18(1)
C(23)	-1740(1)	1371(1)	309(1)	23(1)
C(24)	-3096(1)	1021(1)	327(1)	23(1)
C(25)	-3727(1)	1383(1)	999(1)	21(1)
C(26)	-3002(1)	2096(1)	1660(1)	17(1)
C(27)	62(1)	7791(1)	1780(1)	19(1)
C(28)	-761(1)	8429(1)	1307(1)	25(1)
C(29)	2706(1)	5584(1)	1648(1)	14(1)
C(30)	3278(1)	6670(1)	1325(1)	21(1)

C(31)	4475(1)	6650(1)	982(1)	25(1)
C(32)	5092(1)	5557(2)	961(1)	25(1)
C(33)	4522(1)	4475(1)	1274(1)	24(1)
C(34)	3327(1)	4483(1)	1622(1)	18(1)
C(35)	680(1)	6892(1)	3571(1)	17(1)
C(36)	1010(1)	7426(1)	4357(1)	20(1)
N(1)	4245(1)	2076(1)	2895(1)	22(1)
N(2)	4502(1)	2837(1)	3502(1)	24(1)
N(3)	4720(2)	3596(1)	4033(1)	41(1)
N(4)	5808(1)	638(1)	3728(1)	26(1)
N(5)	6018(1)	-135(1)	4192(1)	25(1)
N(6)	6258(1)	-832(1)	4647(1)	36(1)
N(7)	4522(1)	-384(1)	2184(1)	24(1)
N(8)	5622(1)	-737(1)	2278(1)	24(1)
N(9)	6621(1)	-1100(1)	2297(1)	34(1)
N(10)	2132(1)	284(1)	2348(1)	26(1)
N(11)	2292(1)	773(1)	1732(1)	24(1)
N(12)	2406(2)	1229(1)	1147(1)	37(1)
N(13)	592(1)	4172(1)	2155(1)	15(1)
P(1)	-652(1)	3384(1)	2473(1)	12(1)
P(2)	1205(1)	5615(1)	2136(1)	12(1)

Table S8. Bond lengths [Å] and angles [°] for [PNP][$As(N_3)_4$].

As(1)-N(7)	1.9052(12)
As(1)-N(1)	1.9114(11)
As(1)-N(10)	2.0472(11)
As(1)-N(4)	2.2014(12)
C(1)-C(2)	1.387(2)
C(1)-C(13)	1.390(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.3923(18)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3955(16)
C(3)-H(3)	0.9500
C(4)-C(14)	1.4012(16)
C(4)-P(1)	1.8010(12)
C(5)-C(27)	1.3952(17)
C(5)-C(6)	1.4020(16)
C(5)-P(2)	1.7984(12)
C(6)-C(7)	1.3914(18)
C(6)-H(6)	0.9500
C(7)-C(8)	1.393(2)
C(7)-H(7)	0.9500
C(8)-C(28)	1.384(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.385(2)
C(9)-C(36)	1.3892(19)
C(9)-H(9)	0.9500
C(10)-C(11)	1.3933(18)
C(10)-H(10)	0.9500
C(11)-C(12)	1.4004(17)
C(11)-H(11)	0.9500
C(12)-C(35)	1.3984(17)
C(12)-P(2)	1.7998(12)
C(13)-C(14)	1.3879(18)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500

C(15)-C(16)	1.3976(16)
C(15)-C(20)	1.3980(16)
C(15)-P(1)	1.7923(12)
C(16)-C(17)	1.3929(17)
C(16)-H(16)	0.9500
C(17)-C(18)	1.3910(18)
C(17)-H(17)	0.9500
C(18)-C(19)	1.3892(17)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3910(16)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(26)	1.3976(16)
C(21)-C(22)	1.4013(16)
C(21)-P(1)	1.7986(12)
C(22)-C(23)	1.3890(17)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3913(19)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3902(19)
C(24)-H(24)	0.9500
C(25)-C(26)	1.3924(17)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-C(28)	1.3946(18)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(29)-C(34)	1.3962(17)
C(29)-C(30)	1.3986(17)
C(29)-P(2)	1.7945(12)
C(30)-C(31)	1.3911(18)
C(30)-H(30)	0.9500
C(31)-C(32)	1.387(2)
C(31)-H(31)	0.9500
C(32)-C(33)	1.387(2)
C(32)-H(32)	0.9500

C(33)-C(34)	1.3925(18)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(36)	1.3902(17)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
N(1)-N(2)	1.2322(16)
N(2)-N(3)	1.1355(18)
N(4)-N(5)	1.2113(17)
N(5)-N(6)	1.1491(18)
N(7)-N(8)	1.2322(16)
N(8)-N(9)	1.1348(17)
N(10)-N(11)	1.2149(17)
N(11)-N(12)	1.1447(18)
N(13)-P(2)	1.5822(10)
N(13)-P(1)	1.5862(10)

N(7)-As(1)-N(1)	95.49(5)
N(7)-As(1)-N(10)	84.25(5)
N(1)-As(1)-N(10)	87.19(5)
N(7)-As(1)-N(4)	88.62(5)
N(1)-As(1)-N(4)	83.42(5)
N(10)-As(1)-N(4)	167.62(5)
C(2)-C(1)-C(13)	120.08(12)
C(2)-C(1)-H(1)	120.0
C(13)-C(1)-H(1)	120.0
C(1)-C(2)-C(3)	120.16(12)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(2)-C(3)-C(4)	119.95(12)
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(3)-C(4)-C(14)	119.69(11)
C(3)-C(4)-P(1)	120.53(9)
C(14)-C(4)-P(1)	119.38(9)
C(27)-C(5)-C(6)	119.94(11)

C(27)-C(5)-P(2)	122.68(9)
C(6)-C(5)-P(2)	117.35(9)
C(7)-C(6)-C(5)	119.67(12)
C(7)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
C(6)-C(7)-C(8)	120.17(12)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(28)-C(8)-C(7)	120.18(12)
C(28)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(10)-C(9)-C(36)	120.21(12)
C(10)-C(9)-H(9)	119.9
C(36)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	120.11(12)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	120.04(12)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(35)-C(12)-C(11)	119.40(11)
C(35)-C(12)-P(2)	120.19(9)
C(11)-C(12)-P(2)	120.09(9)
C(14)-C(13)-C(1)	120.25(12)
C(14)-C(13)-H(13)	119.9
C(1)-C(13)-H(13)	119.9
C(13)-C(14)-C(4)	119.85(12)
C(13)-C(14)-H(14)	120.1
C(4)-C(14)-H(14)	120.1
C(16)-C(15)-C(20)	120.21(11)
C(16)-C(15)-P(1)	121.00(9)
C(20)-C(15)-P(1)	118.76(9)
C(17)-C(16)-C(15)	119.65(11)
C(17)-C(16)-H(16)	120.2
C(15)-C(16)-H(16)	120.2
C(18)-C(17)-C(16)	119.99(11)

C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	120.37(11)
C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(20)	120.11(11)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	119.66(11)
C(19)-C(20)-H(20)	120.2
C(15)-C(20)-H(20)	120.2
C(26)-C(21)-C(22)	119.96(11)
C(26)-C(21)-P(1)	121.92(9)
C(22)-C(21)-P(1)	118.12(9)
C(23)-C(22)-C(21)	119.81(11)
C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(22)-C(23)-C(24)	120.09(12)
C(22)-C(23)-H(23)	120.0
C(24)-C(23)-H(23)	120.0
C(25)-C(24)-C(23)	120.27(12)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	120.10(12)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(21)	119.76(11)
C(25)-C(26)-H(26)	120.1
C(21)-C(26)-H(26)	120.1
C(28)-C(27)-C(5)	119.79(12)
C(28)-C(27)-H(27)	120.1
C(5)-C(27)-H(27)	120.1
C(8)-C(28)-C(27)	120.25(13)
C(8)-C(28)-H(28)	119.9
C(27)-C(28)-H(28)	119.9
C(34)-C(29)-C(30)	120.33(11)

C(34)-C(29)-P(2)	119.36(9)
C(30)-C(29)-P(2)	120.26(9)
C(31)-C(30)-C(29)	119.58(12)
C(31)-C(30)-H(30)	120.2
C(29)-C(30)-H(30)	120.2
C(32)-C(31)-C(30)	119.98(13)
C(32)-C(31)-H(31)	120.0
C(30)-C(31)-H(31)	120.0
C(33)-C(32)-C(31)	120.55(12)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(32)-C(33)-C(34)	120.09(13)
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-H(33)	120.0
C(33)-C(34)-C(29)	119.47(12)
C(33)-C(34)-H(34)	120.3
C(29)-C(34)-H(34)	120.3
C(36)-C(35)-C(12)	120.08(11)
C(36)-C(35)-H(35)	120.0
C(12)-C(35)-H(35)	120.0
C(9)-C(36)-C(35)	120.15(12)
C(9)-C(36)-H(36)	119.9
C(35)-C(36)-H(36)	119.9
N(2)-N(1)-As(1)	113.94(9)
N(3)-N(2)-N(1)	175.68(16)
N(5)-N(4)-As(1)	114.99(9)
N(6)-N(5)-N(4)	177.23(14)
N(8)-N(7)-As(1)	117.57(10)
N(9)-N(8)-N(7)	174.15(15)
N(11)-N(10)-As(1)	115.49(9)
N(12)-N(11)-N(10)	178.12(15)
P(2)-N(13)-P(1)	138.69(7)
N(13)-P(1)-C(15)	108.66(5)
N(13)-P(1)-C(21)	109.14(5)
C(15)-P(1)-C(21)	108.66(5)
N(13)-P(1)-C(4)	114.60(5)

C(15)-P(1)-C(4)	107.48(5)
C(21)-P(1)-C(4)	108.16(5)
N(13)-P(2)-C(29)	106.31(5)
N(13)-P(2)-C(5)	112.87(5)
C(29)-P(2)-C(5)	107.86(5)
N(13)-P(2)-C(12)	113.78(5)
C(29)-P(2)-C(12)	106.75(5)
C(5)-P(2)-C(12)	108.90(5)

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3) for [PNP][$As(N_3)_4$]. 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}
As(1)	17(1)	18(1)	18(1)	2(1)	0(1)	1(1)
C(1)	25(1)	22(1)	28(1)	-5(1)	6(1)	7(1)
C(2)	29(1)	25(1)	18(1)	-2(1)	6(1)	5(1)
C(3)	22(1)	19(1)	16(1)	2(1)	2(1)	4(1)
C(4)	14(1)	13(1)	16(1)	0(1)	2(1)	2(1)
C(5)	14(1)	17(1)	13(1)	4(1)	2(1)	3(1)
C(6)	18(1)	24(1)	14(1)	2(1)	1(1)	2(1)
C(7)	18(1)	39(1)	14(1)	7(1)	0(1)	5(1)
C(8)	22(1)	40(1)	22(1)	16(1)	5(1)	14(1)
C(9)	31(1)	23(1)	13(1)	-1(1)	-1(1)	-4(1)
C(10)	21(1)	39(1)	19(1)	-1(1)	-5(1)	-3(1)
C(11)	17(1)	32(1)	17(1)	0(1)	-2(1)	2(1)
C(12)	17(1)	14(1)	12(1)	2(1)	-1(1)	0(1)
C(13)	20(1)	20(1)	29(1)	1(1)	0(1)	8(1)
C(14)	18(1)	18(1)	18(1)	2(1)	0(1)	4(1)
C(15)	15(1)	13(1)	13(1)	2(1)	1(1)	4(1)
C(16)	17(1)	17(1)	19(1)	3(1)	0(1)	1(1)
C(17)	23(1)	17(1)	22(1)	6(1)	3(1)	2(1)
C(18)	22(1)	20(1)	16(1)	6(1)	2(1)	8(1)
C(19)	17(1)	21(1)	15(1)	2(1)	-1(1)	6(1)
C(20)	16(1)	16(1)	16(1)	2(1)	-1(1)	2(1)
C(21)	15(1)	13(1)	13(1)	2(1)	-1(1)	2(1)
C(22)	18(1)	19(1)	16(1)	0(1)	2(1)	2(1)
C(23)	26(1)	24(1)	16(1)	-3(1)	2(1)	2(1)
C(24)	26(1)	21(1)	18(1)	-2(1)	-4(1)	0(1)
C(25)	17(1)	21(1)	22(1)	1(1)	-3(1)	0(1)
C(26)	16(1)	18(1)	17(1)	1(1)	1(1)	1(1)
C(27)	22(1)	18(1)	18(1)	5(1)	2(1)	5(1)
C(28)	30(1)	25(1)	25(1)	10(1)	7(1)	12(1)
C(29)	13(1)	18(1)	11(1)	0(1)	0(1)	1(1)
C(30)	19(1)	22(1)	21(1)	5(1)	4(1)	1(1)

C(31)	20(1)	33(1)	22(1)	7(1)	5(1)	-2(1)
C(32)	15(1)	41(1)	17(1)	-1(1)	2(1)	3(1)
C(33)	18(1)	30(1)	24(1)	-2(1)	0(1)	9(1)
C(34)	17(1)	20(1)	18(1)	1(1)	0(1)	4(1)
C(35)	18(1)	15(1)	16(1)	0(1)	1(1)	1(1)
C(36)	28(1)	17(1)	16(1)	-1(1)	4(1)	0(1)
N(1)	25(1)	18(1)	23(1)	2(1)	0(1)	2(1)
N(2)	19(1)	21(1)	32(1)	2(1)	0(1)	-2(1)
N(3)	45(1)	30(1)	42(1)	-9(1)	0(1)	-10(1)
N(4)	23(1)	29(1)	26(1)	3(1)	-6(1)	2(1)
N(5)	21(1)	24(1)	26(1)	-3(1)	-8(1)	4(1)
N(6)	36(1)	29(1)	43(1)	5(1)	-16(1)	8(1)
N(7)	23(1)	26(1)	22(1)	-2(1)	0(1)	7(1)
N(8)	25(1)	17(1)	28(1)	0(1)	5(1)	2(1)
N(9)	27(1)	27(1)	47(1)	0(1)	6(1)	7(1)
N(10)	19(1)	31(1)	26(1)	2(1)	-3(1)	0(1)
N(11)	23(1)	23(1)	23(1)	-7(1)	-8(1)	8(1)
N(12)	53(1)	35(1)	23(1)	0(1)	-11(1)	11(1)
N(13)	15(1)	13(1)	17(1)	2(1)	2(1)	0(1)
P(1)	12(1)	12(1)	12(1)	1(1)	0(1)	2(1)
P(2)	12(1)	12(1)	11(1)	1(1)	0(1)	1(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)for [PNP][$As(N_3)_4$].

	x	y	z	U(eq)
H(1)	-3516	6688	4124	30
H(2)	-2278	5379	4825	29
H(3)	-1128	3916	4131	23
H(6)	-537	4976	742	22
H(7)	-1890	6073	-54	28
H(8)	-2048	8228	311	31
H(9)	2535	7921	5223	28
H(10)	4176	7218	4466	33
H(11)	3634	6297	3145	27
H(13)	-3661	6499	2724	27
H(14)	-2532	5032	2022	21
H(16)	-1660	899	2914	21
H(17)	-865	-469	3797	24
H(18)	1161	144	4558	22
H(19)	2396	2122	4451	21
H(20)	1646	3471	3543	19
H(22)	-85	2338	948	21
H(23)	-1312	1115	-150	27
H(24)	-3593	533	-123	27
H(25)	-4654	1144	1007	25
H(26)	-3431	2332	2122	20
H(27)	565	8234	2242	23
H(28)	-824	9305	1451	30
H(30)	2852	7417	1340	25
H(31)	4869	7384	761	30
H(32)	5913	5549	730	29
H(33)	4946	3728	1252	28
H(34)	2936	3745	1841	22
H(35)	-210	6816	3345	20
H(36)	344	7707	4669	24

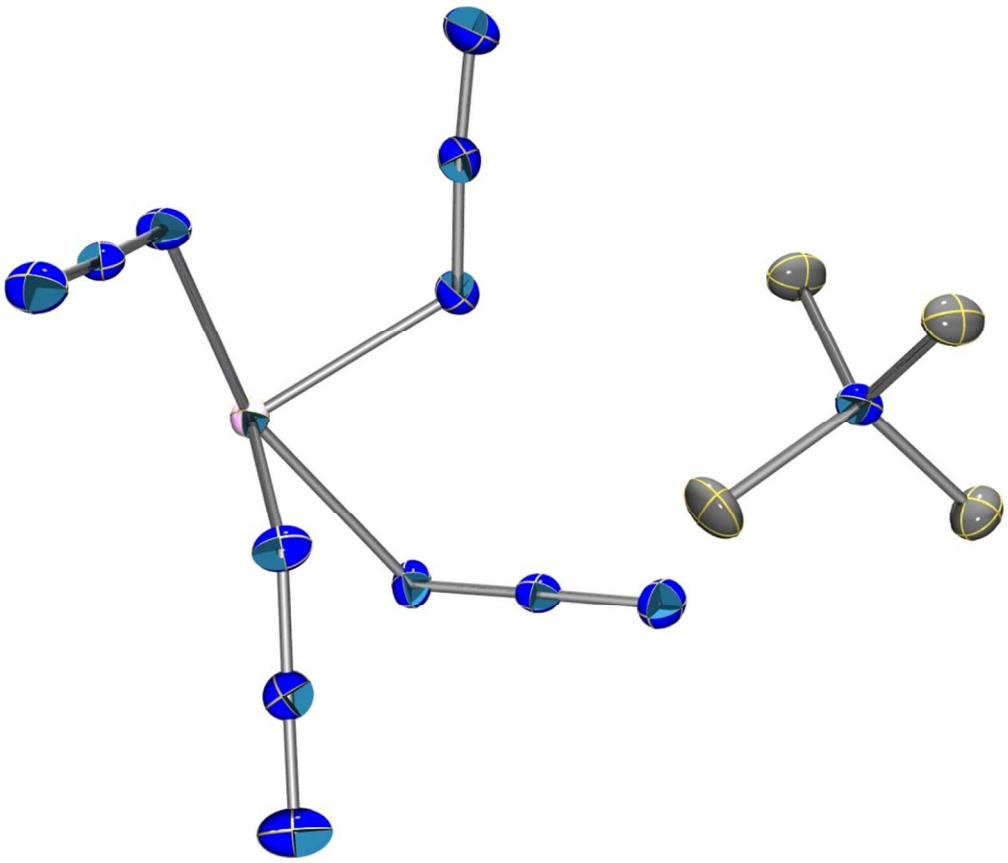

Figure S7: Asymmetric unit in the crystal structure of $[NMe_4][Sb(N_3)_4]$. Thermal ellipsoids are shown at the 50% probability level.

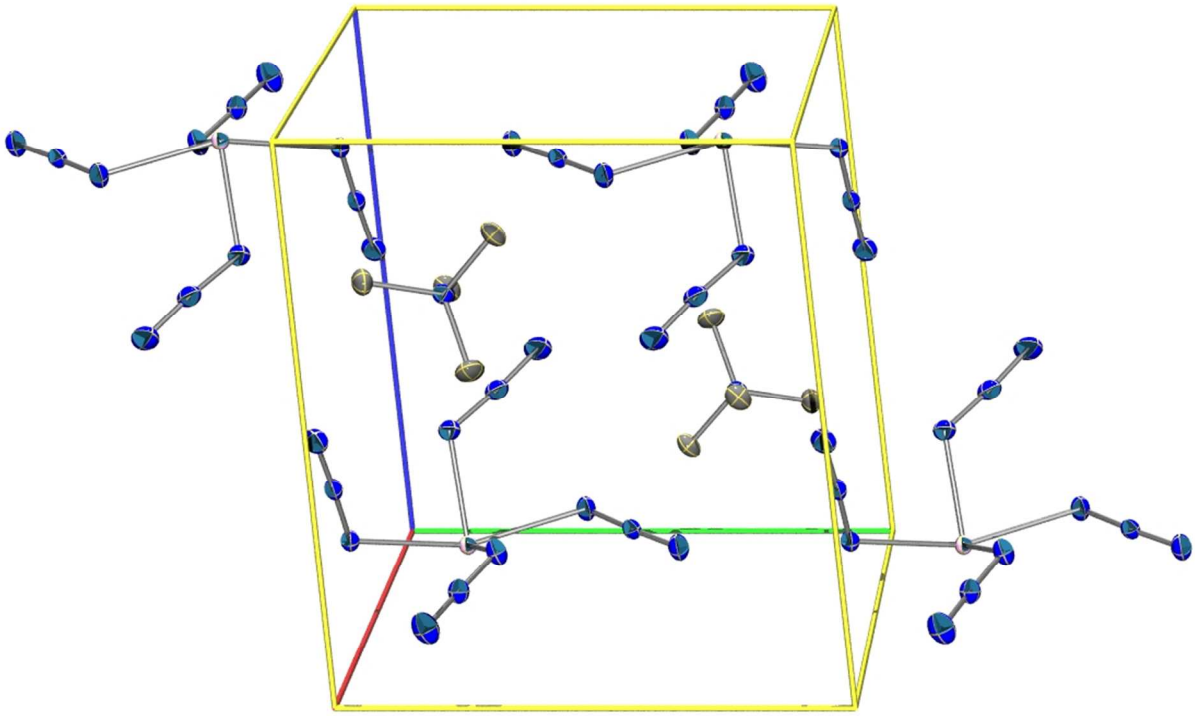

Figure S8: Unit cell of $[NMe_4][Sb(N_3)_4]$. View normal to (100). Thermal ellipsoids are shown at the 50% probability level.

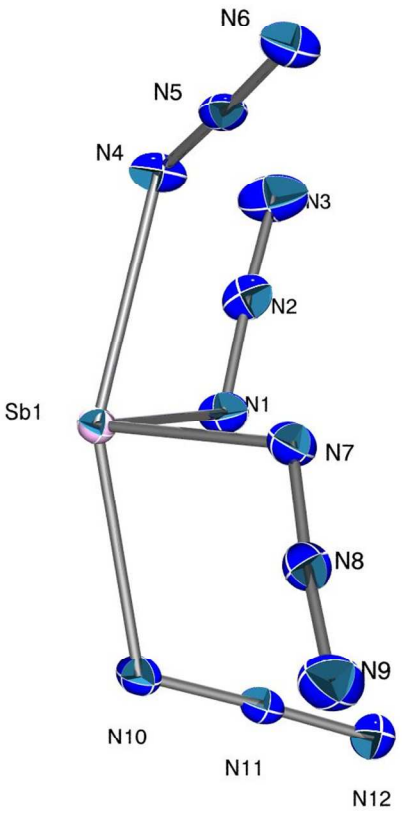

Figure S9: The anion of $[NMe_4][Sb(N_3)_4]$. Thermal ellipsoids are shown at the 50% probability level.

Table S11. Crystal data and structure refinement for $[NMe_4][Sb(N_3)_4]$.

Empirical formula	C4 H12 N13 Sb	
Formula weight	364.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.81250(10) Å	α= 96.3320(10)°.
	b = 9.04720(10) Å	β= 109.9990(10)°.
	c = 9.9380(2) Å	γ = 98.0090(10)°.
Volume	644.150(17) $Å^3$	
Z	2	
Density (calculated)	1.877 Mg/m^3	
Absorption coefficient	2.151 mm^{-1}	
F(000)	356	
Crystal size	0.51 x 0.31 x 0.31 mm^3	
Theta range for data collection	2.21 to 30.55°.	
Index ranges	-11<=h<=10, -12<=k<=12, -14<=l<=14	
Reflections collected	16956	
Independent reflections	3898 [R(int) = 0.0194]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5543 and 0.4061	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3898 / 0 / 168	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0123, wR2 = 0.0327	
R indices (all data)	R1 = 0.0126, wR2 = 0.0329	
Extinction coefficient	0.0155(7)	
Largest diff. peak and hole	0.763 and -0.618 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[NMe_4][Sb(N_3)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3092(2)	7496(1)	3450(1)	20(1)
C(2)	204(2)	5977(1)	1690(1)	19(1)
C(3)	454(2)	6769(2)	4190(1)	25(1)
C(4)	350(2)	8634(1)	2580(1)	20(1)
N(1)	6115(1)	8305(1)	6929(1)	19(1)
N(2)	6737(1)	7363(1)	6356(1)	19(1)
N(3)	7296(2)	6530(1)	5746(1)	30(1)
N(4)	6313(1)	5751(1)	8443(1)	18(1)
N(5)	5205(1)	4703(1)	8472(1)	15(1)
N(6)	4181(1)	3656(1)	8478(1)	20(1)
N(7)	3156(1)	7106(1)	8241(1)	18(1)
N(8)	2079(1)	7748(1)	8615(1)	17(1)
N(9)	982(1)	8271(1)	8915(1)	27(1)
N(10)	4862(1)	10310(1)	8577(1)	17(1)
N(11)	3859(1)	10329(1)	7339(1)	15(1)
N(12)	2926(1)	10390(1)	6179(1)	21(1)
N(13)	1024(1)	7218(1)	2981(1)	14(1)
Sb(1)	5977(1)	8160(1)	9000(1)	12(1)

Table S13. Bond lengths [Å] and angles [°] for $[NMe_4][Sb(N_3)_4]$.

C(1)-N(13)	1.4957(13)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-N(13)	1.4954(13)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-N(13)	1.4937(14)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-N(13)	1.4944(14)
C(4)-H(4C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
N(1)-N(2)	1.2181(13)
N(1)-Sb(1)	2.1149(9)
N(2)-N(3)	1.1397(15)
N(4)-N(5)	1.2018(14)
N(4)-Sb(1)	2.2616(9)
N(5)-N(6)	1.1536(14)
N(7)-N(8)	1.2186(13)
N(7)-Sb(1)	2.1109(9)
N(8)-N(9)	1.1415(14)
N(10)-N(11)	1.2157(13)
N(10)-Sb(1)	2.2635(9)
N(11)-N(12)	1.1460(14)

N(13)-C(1)-H(1A)	109.5
N(13)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(13)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

N(13)-C(2)-H(2A)	109.5
N(13)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
N(13)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
N(13)-C(3)-H(3A)	109.5
N(13)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
N(13)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(13)-C(4)-H(4C)	109.5
N(13)-C(4)-H(4A)	109.5
H(4C)-C(4)-H(4A)	109.5
N(13)-C(4)-H(4B)	109.5
H(4C)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
N(2)-N(1)-Sb(1)	120.13(8)
N(3)-N(2)-N(1)	175.59(12)
N(5)-N(4)-Sb(1)	120.44(7)
N(6)-N(5)-N(4)	177.11(10)
N(8)-N(7)-Sb(1)	118.77(8)
N(9)-N(8)-N(7)	175.57(12)
N(11)-N(10)-Sb(1)	116.61(7)
N(12)-N(11)-N(10)	178.06(11)
C(3)-N(13)-C(4)	109.56(9)
C(3)-N(13)-C(2)	109.49(9)
C(4)-N(13)-C(2)	109.45(8)
C(3)-N(13)-C(1)	109.89(9)
C(4)-N(13)-C(1)	109.21(9)
C(2)-N(13)-C(1)	109.22(8)
N(7)-Sb(1)-N(1)	96.26(4)
N(7)-Sb(1)-N(4)	81.67(4)
N(1)-Sb(1)-N(4)	82.48(4)
N(7)-Sb(1)-N(10)	84.70(4)

N(1)-Sb(1)-N(10)	79.61(3)
N(4)-Sb(1)-N(10)	156.11(4)

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[NMe_4][Sb(N_3)_4]$. 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}
C(1)	12(1)	23(1)	22(1)	-2(1)	4(1)	2(1)
C(2)	17(1)	18(1)	19(1)	-4(1)	5(1)	1(1)
C(3)	31(1)	27(1)	22(1)	7(1)	16(1)	2(1)
C(4)	23(1)	16(1)	21(1)	3(1)	5(1)	6(1)
N(1)	24(1)	20(1)	17(1)	6(1)	10(1)	8(1)
N(2)	21(1)	22(1)	18(1)	8(1)	10(1)	7(1)
N(3)	44(1)	33(1)	29(1)	12(1)	25(1)	21(1)
N(4)	20(1)	13(1)	25(1)	3(1)	13(1)	4(1)
N(5)	17(1)	14(1)	15(1)	2(1)	8(1)	7(1)
N(6)	22(1)	14(1)	27(1)	2(1)	13(1)	3(1)
N(7)	15(1)	14(1)	24(1)	-1(1)	7(1)	2(1)
N(8)	16(1)	15(1)	20(1)	2(1)	6(1)	1(1)
N(9)	21(1)	25(1)	37(1)	0(1)	14(1)	5(1)
N(10)	24(1)	13(1)	14(1)	2(1)	5(1)	5(1)
N(11)	16(1)	11(1)	17(1)	1(1)	8(1)	3(1)
N(12)	21(1)	22(1)	18(1)	1(1)	4(1)	7(1)
N(13)	13(1)	15(1)	14(1)	2(1)	6(1)	2(1)
Sb(1)	13(1)	11(1)	12(1)	2(1)	4(1)	2(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[NMe_4][Sb(N_3)_4]$.

	x	y	z	U(eq)
H(1A)	3544	6582	3748	30
H(1B)	3633	8339	4269	30
H(1C)	3454	7750	2639	30
H(2A)	-1150	5769	1400	29
H(2B)	686	5061	1941	29
H(2C)	537	6289	885	29
H(3A)	919	5852	4465	37
H(3B)	-902	6569	3870	37
H(3C)	973	7590	5029	37
H(4C)	880	9446	3428	30
H(4D)	-1007	8452	2257	30
H(4E)	733	8932	1792	30

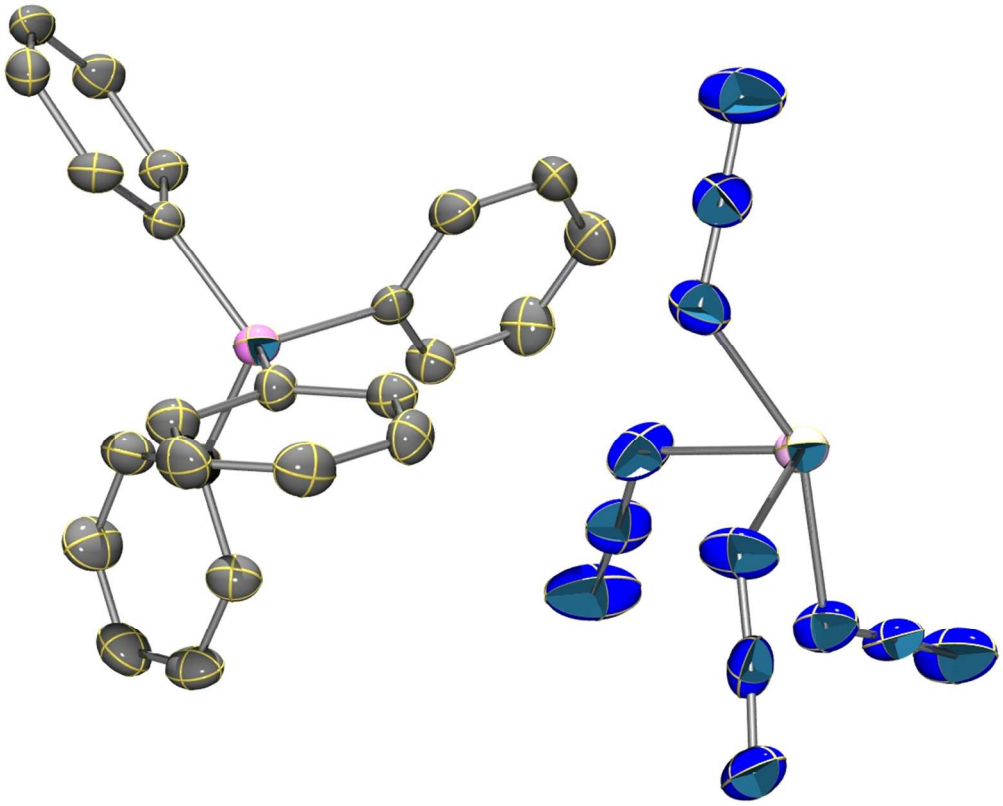

Figure S10: Asymmetric unit in the crystal structure of $[PPh_4][Sb(N_3)_4]$. Thermal ellipsoids are shown at the 50% probability level.

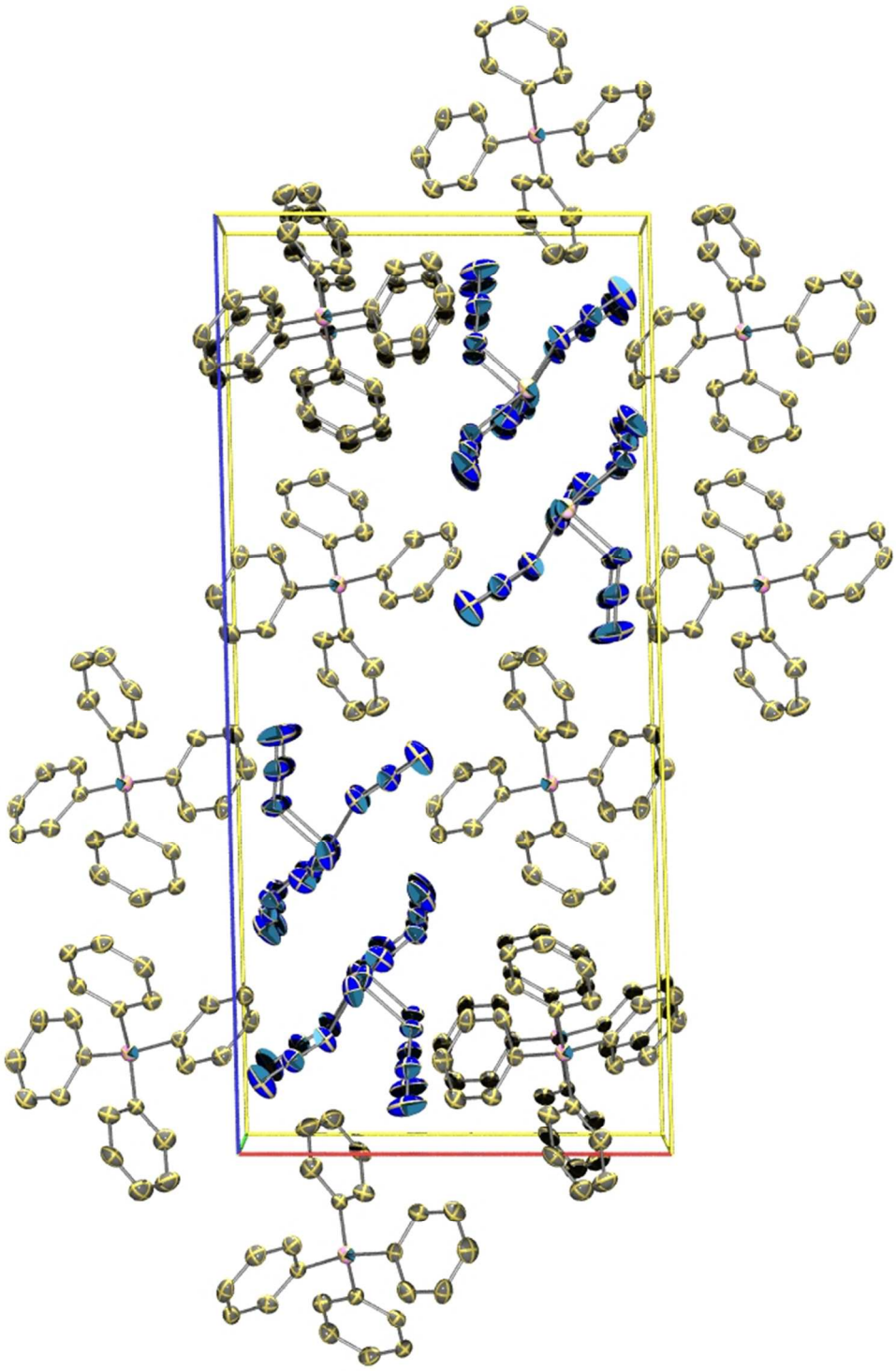

Figure S11: Unit cell of $[PPh_4][Sb(N_3)_4]$. View normal to (010). Thermal ellipsoids are shown at the 50% probability level.

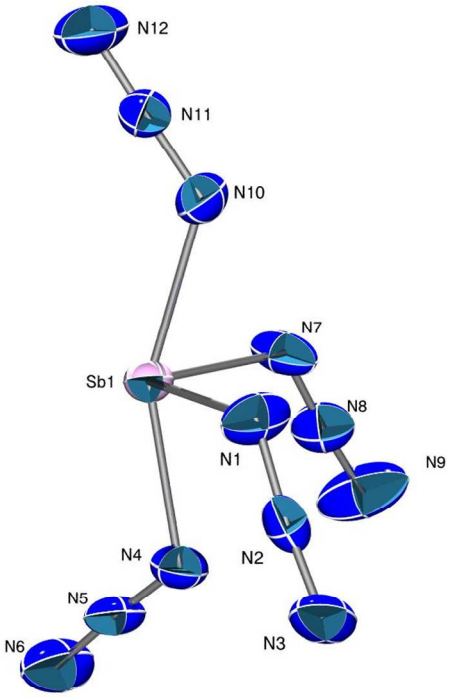

Figure S12: The anion of $[PPh_4][Sb(N_3)_4]$. Thermal ellipsoids are shown at the 50% probability level.

Table S16. Crystal data and structure refinement for $[PPh_4][Sb(N_3)_4]$.

Identification code	tppsbn1_0m	
Empirical formula	C24 H20 N12 P Sb	
Formula weight	629.24	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.7508(13) Å	α= 90°.
	b = 7.3433(8) Å	β= 91.411(2)°.
	c = 27.749(3) Å	γ = 90°.
Volume	2597.4(5) $Å^3$	
Z	4	
Density (calculated)	1.609 Mg/m^3	
Absorption coefficient	1.163 mm^{-1}	
F(000)	1256	
Crystal size	0.22 x 0.06 x 0.05 mm^3	
Theta range for data collection	1.47 to 26.37°.	
Index ranges	-15<=h<=12, -8<=k<=9, -34<=l<=34	
Reflections collected	15017	
Independent reflections	5205 [R(int) = 0.0713]	
Completeness to theta = 26.37°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9441 and 0.7839	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5205 / 0 / 343	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.0785	
R indices (all data)	R1 = 0.0916, wR2 = 0.0928	
Largest diff. peak and hole	0.856 and -0.486 e.$Å^{-3}$	

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4][Sb(N_3)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7395(4)	8087(6)	1566(2)	24(1)
C(2)	6452(4)	8016(6)	1808(2)	27(1)
C(3)	6322(4)	6716(6)	2170(2)	29(1)
C(4)	7128(4)	5545(6)	2284(2)	32(1)
C(5)	8065(4)	5606(6)	2041(2)	32(1)
C(6)	8189(4)	6866(6)	1678(2)	28(1)
C(7)	7718(4)	8372(6)	540(2)	24(1)
C(8)	7157(4)	6750(6)	488(2)	32(1)
C(9)	7230(4)	5742(7)	65(2)	37(1)
C(10)	7862(4)	6341(7)	-297(2)	44(2)
C(11)	8400(5)	7937(8)	-247(2)	48(2)
C(12)	8340(4)	8959(7)	172(2)	38(1)
C(13)	8671(3)	11136(6)	1200(1)	21(1)
C(14)	9394(4)	10846(6)	1573(2)	28(1)
C(15)	10210(4)	12071(7)	1647(2)	31(1)
C(16)	10295(4)	13578(6)	1352(2)	32(1)
C(17)	9579(4)	13858(7)	979(2)	32(1)
C(18)	8765(4)	12656(6)	907(2)	28(1)
C(19)	6449(4)	11141(6)	1021(2)	24(1)
C(20)	5878(4)	11229(7)	588(2)	32(1)
C(21)	5035(4)	12444(7)	546(2)	42(1)
C(22)	4765(4)	13508(7)	932(2)	42(1)
C(23)	5347(4)	13438(7)	1363(2)	38(1)
C(24)	6183(4)	12262(6)	1403(2)	35(1)
N(1)	3389(4)	6427(6)	2112(2)	48(1)
N(2)	3049(3)	5005(7)	1944(2)	35(1)
N(3)	2801(4)	3597(6)	1813(2)	50(1)
N(4)	2097(4)	7203(6)	1260(2)	43(1)
N(5)	1346(4)	7731(6)	1035(2)	42(1)
N(6)	622(4)	8170(7)	808(2)	70(2)
N(7)	4069(3)	9145(6)	1343(1)	49(1)

N(8)	3967(4)	8557(6)	938(2)	45(1)
N(9)	3933(5)	8018(7)	553(2)	80(2)
N(10)	4212(3)	9750(6)	2335(1)	41(1)
N(11)	4271(3)	11214(7)	2518(1)	39(1)
N(12)	4350(4)	12589(7)	2712(2)	72(2)
P(1)	7565(1)	9676(2)	1083(1)	24(1)
Sb(1)	2884(1)	8918(1)	1837(1)	31(1)

Table S18. Bond lengths [Å] and angles [°] for $[PPh_4][Sb(N_3)_4]$.

C(1)-C(6)	1.382(6)
C(1)-C(2)	1.393(6)
C(1)-P(1)	1.794(4)
C(2)-C(3)	1.398(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.370(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.379(6)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(12)	1.379(6)
C(7)-C(8)	1.395(6)
C(7)-P(1)	1.801(4)
C(8)-C(9)	1.392(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.375(7)
C(9)-H(9)	0.9500
C(10)-C(11)	1.364(7)
C(10)-H(10)	0.9500
C(11)-C(12)	1.386(6)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.385(6)
C(13)-C(18)	1.387(6)
C(13)-P(1)	1.794(4)
C(14)-C(15)	1.387(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.382(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.379(6)
C(16)-H(16)	0.9500
C(17)-C(18)	1.373(6)
C(17)-H(17)	0.9500

C(18)-H(18)	0.9500
C(19)-C(20)	1.391(6)
C(19)-C(24)	1.391(6)
C(19)-P(1)	1.789(5)
C(20)-C(21)	1.399(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.375(6)
C(21)-H(21)	0.9500
C(22)-C(23)	1.392(7)
C(22)-H(22)	0.9500
C(23)-C(24)	1.375(6)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
N(1)-N(2)	1.220(5)
N(1)-Sb(1)	2.078(4)
N(2)-N(3)	1.137(5)
N(4)-N(5)	1.195(6)
N(4)-Sb(1)	2.254(4)
N(5)-N(6)	1.150(6)
N(7)-N(8)	1.209(6)
N(7)-Sb(1)	2.071(4)
N(8)-N(9)	1.137(5)
N(10)-N(11)	1.189(5)
N(10)-Sb(1)	2.244(4)
N(11)-N(12)	1.148(6)

C(6)-C(1)-C(2)	120.2(4)
C(6)-C(1)-P(1)	119.2(4)
C(2)-C(1)-P(1)	120.4(4)
C(1)-C(2)-C(3)	119.4(4)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	119.6(5)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	121.1(5)

C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(6)-C(5)-C(4)	119.5(5)
C(6)-C(5)-H(5)	120.3
C(4)-C(5)-H(5)	120.3
C(5)-C(6)-C(1)	120.2(5)
C(5)-C(6)-H(6)	119.9
C(1)-C(6)-H(6)	119.9
C(12)-C(7)-C(8)	119.5(4)
C(12)-C(7)-P(1)	122.0(4)
C(8)-C(7)-P(1)	118.4(4)
C(9)-C(8)-C(7)	119.8(5)
C(9)-C(8)-H(8)	120.1
C(7)-C(8)-H(8)	120.1
C(10)-C(9)-C(8)	119.9(5)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	120.2(5)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	120.8(5)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
C(7)-C(12)-C(11)	119.8(5)
C(7)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(14)-C(13)-C(18)	119.6(4)
C(14)-C(13)-P(1)	123.3(4)
C(18)-C(13)-P(1)	117.0(3)
C(13)-C(14)-C(15)	119.7(4)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(16)-C(15)-C(14)	120.0(5)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.3(5)

C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(18)-C(17)-C(16)	119.7(5)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	120.6(4)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(20)-C(19)-C(24)	119.9(5)
C(20)-C(19)-P(1)	120.7(4)
C(24)-C(19)-P(1)	119.4(3)
C(19)-C(20)-C(21)	119.1(5)
C(19)-C(20)-H(20)	120.5
C(21)-C(20)-H(20)	120.5
C(22)-C(21)-C(20)	120.3(5)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(21)-C(22)-C(23)	120.6(5)
C(21)-C(22)-H(22)	119.7
C(23)-C(22)-H(22)	119.7
C(24)-C(23)-C(22)	119.3(5)
C(24)-C(23)-H(23)	120.4
C(22)-C(23)-H(23)	120.4
C(23)-C(24)-C(19)	120.9(5)
C(23)-C(24)-H(24)	119.6
C(19)-C(24)-H(24)	119.6
N(2)-N(1)-Sb(1)	120.6(3)
N(3)-N(2)-N(1)	173.5(5)
N(5)-N(4)-Sb(1)	121.8(4)
N(6)-N(5)-N(4)	177.1(6)
N(8)-N(7)-Sb(1)	121.6(4)
N(9)-N(8)-N(7)	176.0(6)
N(11)-N(10)-Sb(1)	123.2(3)
N(12)-N(11)-N(10)	176.8(5)
C(19)-P(1)-C(13)	106.2(2)
C(19)-P(1)-C(1)	110.6(2)

C(13)-P(1)-C(1)	111.3(2)
C(19)-P(1)-C(7)	109.9(2)
C(13)-P(1)-C(7)	111.6(2)
C(1)-P(1)-C(7)	107.3(2)
N(7)-Sb(1)-N(1)	95.10(19)
N(7)-Sb(1)-N(10)	80.46(16)
N(1)-Sb(1)-N(10)	77.96(17)
N(7)-Sb(1)-N(4)	83.90(16)
N(1)-Sb(1)-N(4)	84.12(16)
N(10)-Sb(1)-N(4)	154.96(16)

Table S19. Anisotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4][Sb(N_3)_4]$. 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}
C(1)	24(3)	26(3)	21(2)	-1(2)	0(2)	0(2)
C(2)	27(3)	28(3)	25(3)	-2(2)	-4(2)	3(2)
C(3)	23(3)	38(3)	25(3)	1(2)	3(2)	-4(3)
C(4)	38(4)	27(3)	31(3)	2(2)	2(3)	-2(3)
C(5)	31(3)	25(3)	39(3)	3(2)	-5(2)	9(2)
C(6)	26(3)	28(3)	31(3)	-1(2)	1(2)	-1(2)
C(7)	20(3)	30(3)	22(2)	0(2)	-5(2)	-1(2)
C(8)	36(4)	31(3)	27(3)	2(2)	-4(2)	-1(3)
C(9)	46(4)	28(3)	36(3)	-4(2)	-17(3)	1(3)
C(10)	48(4)	45(4)	39(3)	-11(3)	3(3)	6(3)
C(11)	52(4)	55(4)	36(3)	-11(3)	15(3)	-3(3)
C(12)	40(4)	34(3)	41(3)	-6(3)	4(3)	-4(3)
C(13)	19(3)	21(2)	24(2)	-5(2)	5(2)	-2(2)
C(14)	29(3)	27(3)	29(3)	-6(2)	-2(2)	0(2)
C(15)	21(3)	39(3)	34(3)	-10(2)	-4(2)	5(3)
C(16)	24(3)	29(3)	45(3)	-11(2)	6(3)	-8(2)
C(17)	33(3)	26(3)	37(3)	-1(2)	6(2)	-8(3)
C(18)	27(3)	27(3)	30(3)	-1(2)	-1(2)	-2(2)
C(19)	23(3)	19(2)	29(3)	1(2)	1(2)	-3(2)
C(20)	34(3)	33(3)	27(3)	2(2)	-2(2)	1(3)
C(21)	41(4)	48(4)	37(3)	4(3)	-9(3)	6(3)
C(22)	38(4)	34(3)	54(4)	4(3)	-2(3)	7(3)
C(23)	30(4)	31(3)	52(3)	-12(2)	1(3)	0(3)
C(24)	31(4)	32(3)	41(3)	-4(2)	-9(3)	-1(3)
N(1)	65(4)	23(3)	54(3)	3(2)	-19(3)	2(2)
N(2)	25(3)	35(3)	45(3)	10(2)	3(2)	3(2)
N(3)	42(3)	29(3)	79(4)	1(3)	-15(3)	-7(3)
N(4)	38(3)	39(3)	52(3)	-6(2)	-14(2)	-3(2)
N(5)	46(4)	32(3)	47(3)	-5(2)	-9(3)	-11(3)
N(6)	70(4)	46(3)	91(4)	-5(3)	-40(3)	7(3)
N(7)	40(3)	76(4)	30(2)	-6(2)	-1(2)	-22(3)

N(8)	53(3)	40(3)	43(3)	6(2)	3(3)	-12(2)
N(9)	130(6)	75(4)	37(3)	-14(3)	21(3)	-41(4)
N(10)	44(3)	38(3)	40(3)	-9(2)	-9(2)	9(2)
N(11)	37(3)	46(3)	33(2)	-6(2)	-11(2)	7(3)
N(12)	75(4)	53(4)	86(4)	-29(3)	-44(3)	16(3)
P(1)	24(1)	22(1)	24(1)	0(1)	-2(1)	-1(1)
Sb(1)	32(1)	27(1)	33(1)	-1(1)	-4(1)	-2(1)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4][Sb(N_3)_4]$.

	x	y	z	U(eq)
H(2)	5901	8842	1728	32
H(3)	5681	6645	2336	35
H(4)	7043	4676	2534	39
H(5)	8617	4787	2124	38
H(6)	8821	6894	1505	34
H(8)	6727	6335	740	38
H(9)	6845	4642	27	44
H(10)	7923	5641	-583	53
H(11)	8822	8354	-502	57
H(12)	8727	10061	204	46
H(14)	9331	9815	1777	34
H(15)	10712	11874	1901	38
H(16)	10849	14424	1407	39
H(17)	9649	14879	772	38
H(18)	8262	12868	655	33
H(20)	6058	10475	324	38
H(21)	4648	12534	251	50
H(22)	4177	14298	904	50
H(23)	5167	14194	1626	45
H(24)	6585	12214	1696	42

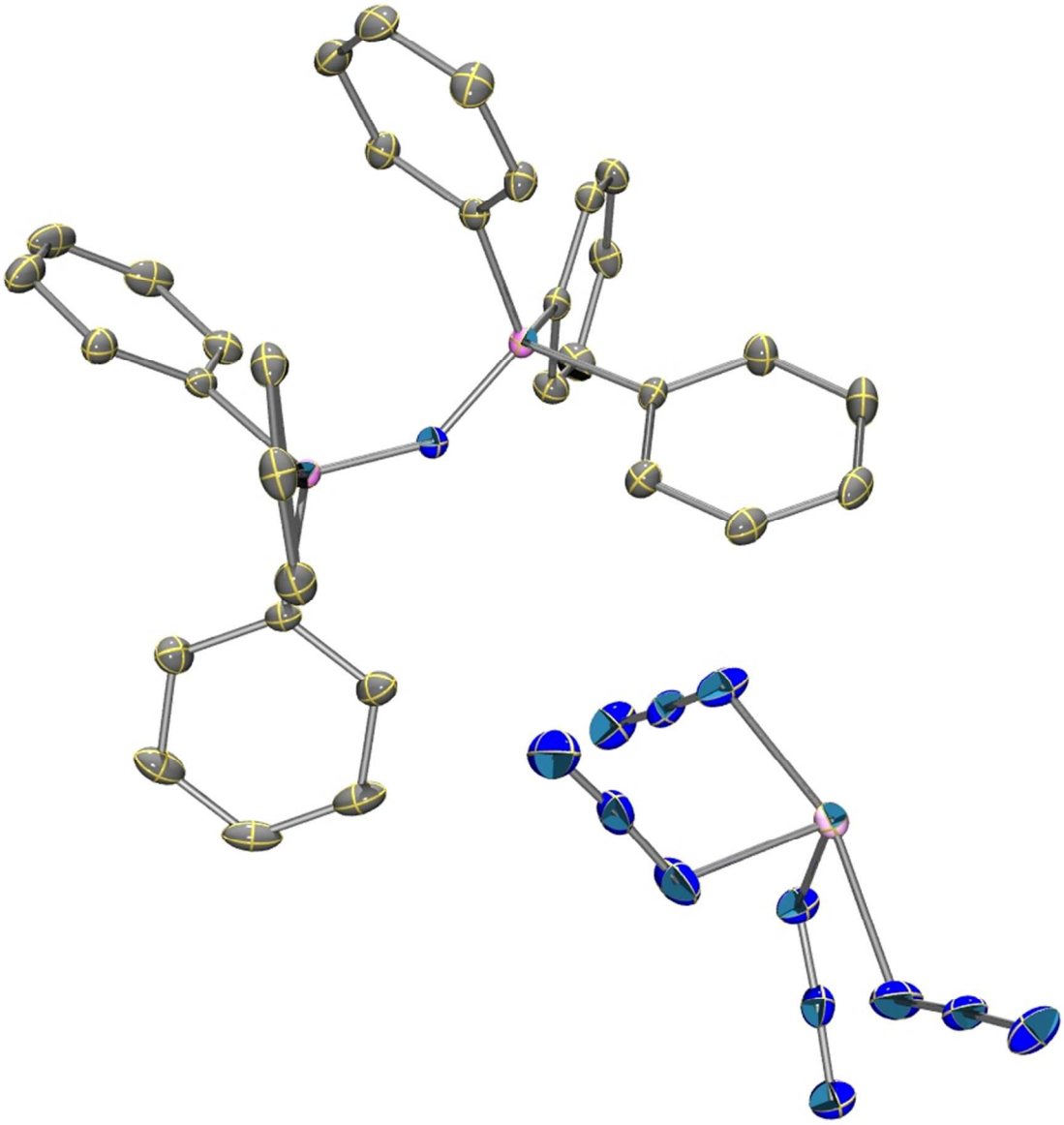

Figure S13: Asymmetric unit in the crystal structure of [PNP][$Sb(N_3)_4$]. Thermal ellipsoids are shown at the 50% probability level.

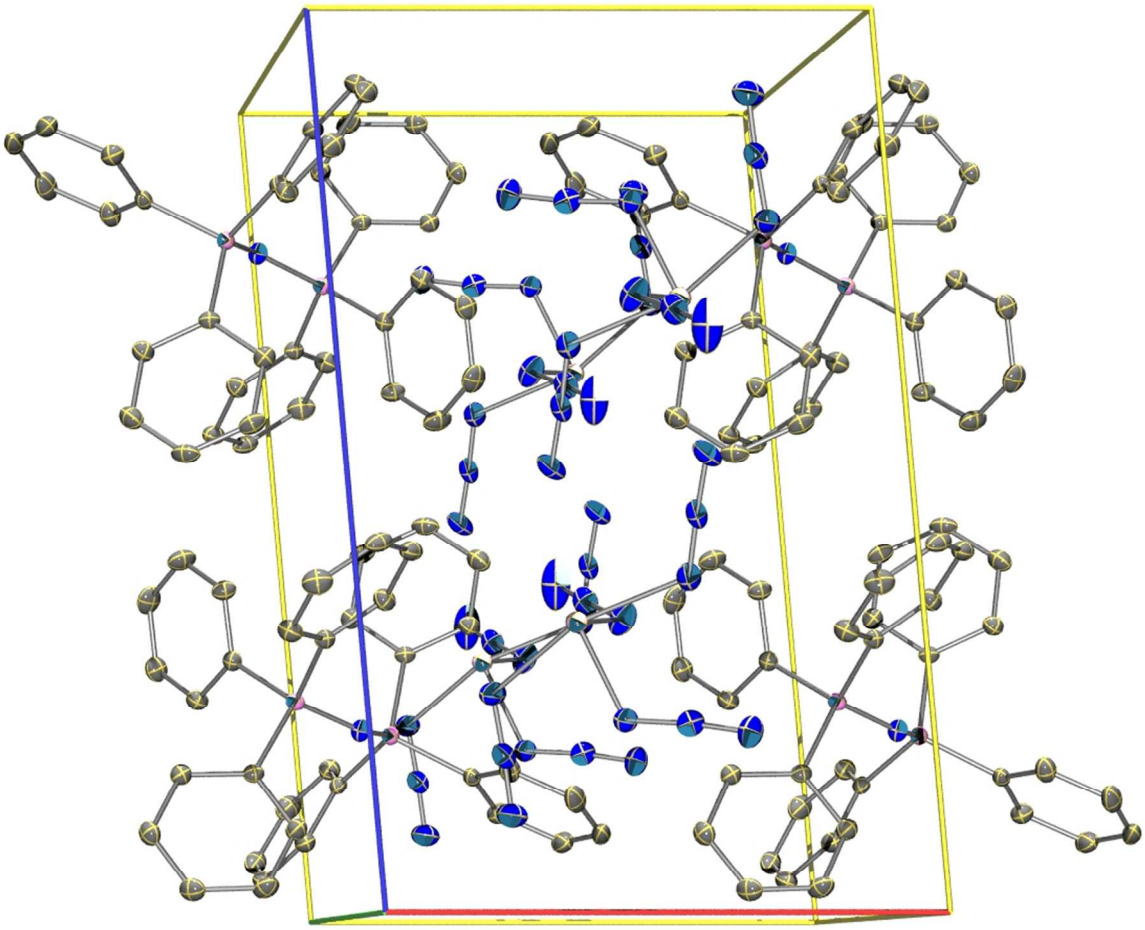

Figure S14: Unit cell of [PNP][$Sb(N_3)_4$]. View normal to (010). Thermal ellipsoids are shown at the 50% probability level.

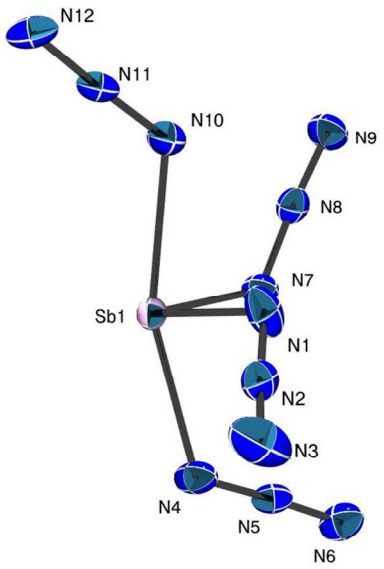

Figure S15: The anion of [PNP][$Sb(N_3)_4$]. Thermal ellipsoids are shown at the 50% probability level.

Table S21. Crystal data and structure refinement for [PNP][$Sb(N_3)_4$].

Empirical formula	C36 H30 N13 P2 Sb	
Formula weight	828.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3792(4) Å	α= 95.1460(10)°.
	b = 10.6043(4) Å	β= 94.9940(10)°.
	c = 16.7458(7) Å	γ = 100.5720(10)°.
Volume	1794.41(12) $Å^3$	
Z	2	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	0.906 mm^{-1}	
F(000)	836	
Crystal size	0.20 x 0.19 x 0.09 mm^3	
Theta range for data collection	1.97 to 30.61°.	
Index ranges	-14<=h<=14, -15<=k<=15, -23<=l<=23	
Reflections collected	29102	
Independent reflections	10971 [R(int) = 0.0440]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9237 and 0.8424	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10971 / 0 / 469	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0681	
R indices (all data)	R1 = 0.0544, wR2 = 0.0746	
Largest diff. peak and hole	0.504 and -0.735 $e.Å^{-3}$	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [PNP][$Sb(N_3)_4$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7455(2)	2453(2)	5253(1)	21(1)
C(2)	6577(2)	2975(2)	5699(1)	22(1)
C(3)	6953(2)	3463(2)	6502(1)	18(1)
C(4)	8222(2)	3452(2)	6856(1)	13(1)
C(5)	11804(2)	7412(2)	8390(1)	14(1)
C(6)	11168(2)	7832(2)	9042(1)	18(1)
C(7)	11904(2)	8566(2)	9710(1)	21(1)
C(8)	13266(2)	8871(2)	9740(1)	20(1)
C(9)	11239(2)	1930(3)	9305(1)	28(1)
C(10)	10433(2)	1315(2)	8628(1)	27(1)
C(11)	9653(2)	1996(2)	8182(1)	19(1)
C(12)	9694(2)	3300(2)	8408(1)	15(1)
C(13)	7310(2)	4397(2)	8344(1)	15(1)
C(14)	6781(2)	5504(2)	8291(1)	22(1)
C(15)	5626(2)	5596(2)	8635(2)	28(1)
C(16)	5004(2)	4596(3)	9020(1)	28(1)
C(17)	5538(2)	3502(3)	9092(1)	27(1)
C(18)	6698(2)	3396(2)	8750(1)	21(1)
C(19)	10310(2)	7573(2)	6864(1)	14(1)
C(20)	11088(2)	8780(2)	6824(1)	20(1)
C(21)	10642(2)	9624(2)	6323(1)	24(1)
C(22)	9430(2)	9251(2)	5859(1)	21(1)
C(23)	8675(2)	8042(2)	5884(1)	21(1)
C(24)	9100(2)	7194(2)	6389(1)	18(1)
C(25)	11777(2)	5495(2)	7020(1)	14(1)
C(26)	12403(2)	4658(2)	7445(1)	18(1)
C(27)	13030(2)	3787(2)	7041(1)	22(1)
C(28)	13053(2)	3758(2)	6212(1)	24(1)
C(29)	12457(2)	4601(2)	5791(1)	24(1)
C(30)	11815(2)	5465(2)	6190(1)	18(1)
C(31)	13900(2)	8461(2)	9098(1)	19(1)

C(32)	13168(2)	7745(2)	8415(1)	16(1)
C(33)	8718(2)	2464(2)	5592(1)	20(1)
C(34)	9112(2)	2961(2)	6392(1)	17(1)
C(35)	10508(2)	3913(2)	9103(1)	19(1)
C(36)	11271(2)	3224(2)	9548(1)	26(1)
N(1)	4947(2)	8038(2)	6652(1)	32(1)
N(2)	5412(2)	7115(2)	6405(1)	26(1)
N(3)	5750(2)	6214(2)	6161(2)	52(1)
N(4)	7603(2)	9076(2)	7548(1)	30(1)
N(5)	7469(2)	8910(2)	8242(1)	21(1)
N(6)	7390(2)	8743(2)	8905(1)	30(1)
N(7)	5528(2)	10383(2)	7900(1)	23(1)
N(8)	4464(2)	10728(2)	7946(1)	22(1)
N(9)	3497(2)	11046(2)	8050(1)	30(1)
N(10)	4194(2)	10393(2)	6309(1)	33(1)
N(11)	4018(2)	10655(2)	5634(1)	23(1)
N(12)	3802(2)	10926(2)	4990(1)	28(1)
N(13)	9527(2)	5693(2)	7845(1)	16(1)
P(1)	8760(1)	4268(1)	7855(1)	12(1)
P(2)	10802(1)	6479(1)	7537(1)	13(1)
Sb(1)	6139(1)	9882(1)	6783(1)	18(1)

Table S23. Bond lengths [Å] and angles [°] for [PNP][$Sb(N_3)_4$].

C(1)-C(33)	1.380(3)
C(1)-C(2)	1.387(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.393(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.399(3)
C(3)-H(3)	0.9500
C(4)-C(34)	1.399(3)
C(4)-P(1)	1.805(2)
C(5)-C(32)	1.391(3)
C(5)-C(6)	1.404(3)
C(5)-P(2)	1.792(2)
C(6)-C(7)	1.385(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.387(3)
C(7)-H(7)	0.9500
C(8)-C(31)	1.386(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.384(3)
C(9)-C(36)	1.390(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.393(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.393(3)
C(11)-H(11)	0.9500
C(12)-C(35)	1.407(3)
C(12)-P(1)	1.797(2)
C(13)-C(14)	1.391(3)
C(13)-C(18)	1.397(3)
C(13)-P(1)	1.795(2)
C(14)-C(15)	1.390(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.378(4)
C(15)-H(15)	0.9500

C(16)-C(17)	1.384(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.395(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.393(3)
C(19)-C(24)	1.398(3)
C(19)-P(2)	1.796(2)
C(20)-C(21)	1.393(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.391(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.380(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.392(3)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-C(30)	1.392(3)
C(25)-C(26)	1.400(3)
C(25)-P(2)	1.801(2)
C(26)-C(27)	1.385(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.387(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.385(3)
C(28)-H(28)	0.9500
C(29)-C(30)	1.386(3)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(32)	1.393(3)
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500
C(33)-C(34)	1.393(3)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(36)	1.387(3)

C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
N(1)-N(2)	1.223(3)
N(1)-Sb(1)	2.096(2)
N(2)-N(3)	1.132(3)
N(4)-N(5)	1.206(3)
N(4)-Sb(1)	2.240(2)
N(5)-N(6)	1.148(3)
N(7)-N(8)	1.232(3)
N(7)-Sb(1)	2.0817(19)
N(8)-N(9)	1.139(3)
N(10)-N(11)	1.195(3)
N(10)-Sb(1)	2.280(2)
N(11)-N(12)	1.155(3)
N(13)-P(1)	1.5763(18)
N(13)-P(2)	1.5817(18)

C(33)-C(1)-C(2)	120.3(2)
C(33)-C(1)-H(1)	119.9
C(2)-C(1)-H(1)	119.9
C(1)-C(2)-C(3)	119.9(2)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	120.2(2)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(34)-C(4)-C(3)	119.34(19)
C(34)-C(4)-P(1)	120.63(16)
C(3)-C(4)-P(1)	119.47(15)
C(32)-C(5)-C(6)	119.91(19)
C(32)-C(5)-P(2)	122.21(16)
C(6)-C(5)-P(2)	117.87(16)
C(7)-C(6)-C(5)	119.8(2)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	120.1(2)

C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(31)-C(8)-C(7)	120.4(2)
C(31)-C(8)-H(8)	119.8
C(7)-C(8)-H(8)	119.8
C(10)-C(9)-C(36)	120.4(2)
C(10)-C(9)-H(9)	119.8
C(36)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	120.0(2)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.2(2)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(35)	119.24(19)
C(11)-C(12)-P(1)	123.43(16)
C(35)-C(12)-P(1)	117.33(16)
C(14)-C(13)-C(18)	120.3(2)
C(14)-C(13)-P(1)	118.58(17)
C(18)-C(13)-P(1)	121.09(16)
C(15)-C(14)-C(13)	119.4(2)
C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3
C(16)-C(15)-C(14)	120.4(2)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	120.7(2)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	119.6(2)
C(16)-C(17)-H(17)	120.2
C(18)-C(17)-H(17)	120.2
C(17)-C(18)-C(13)	119.6(2)
C(17)-C(18)-H(18)	120.2
C(13)-C(18)-H(18)	120.2
C(20)-C(19)-C(24)	120.34(19)

C(20)-C(19)-P(2)	121.51(16)
C(24)-C(19)-P(2)	118.13(16)
C(19)-C(20)-C(21)	119.7(2)
C(19)-C(20)-H(20)	120.1
C(21)-C(20)-H(20)	120.1
C(22)-C(21)-C(20)	119.8(2)
C(22)-C(21)-H(21)	120.1
C(20)-C(21)-H(21)	120.1
C(23)-C(22)-C(21)	120.4(2)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(22)-C(23)-C(24)	120.4(2)
C(22)-C(23)-H(23)	119.8
C(24)-C(23)-H(23)	119.8
C(23)-C(24)-C(19)	119.2(2)
C(23)-C(24)-H(24)	120.4
C(19)-C(24)-H(24)	120.4
C(30)-C(25)-C(26)	119.40(19)
C(30)-C(25)-P(2)	120.80(16)
C(26)-C(25)-P(2)	119.52(16)
C(27)-C(26)-C(25)	120.4(2)
C(27)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
C(26)-C(27)-C(28)	119.7(2)
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-H(27)	120.1
C(29)-C(28)-C(27)	120.2(2)
C(29)-C(28)-H(28)	119.9
C(27)-C(28)-H(28)	119.9
C(28)-C(29)-C(30)	120.4(2)
C(28)-C(29)-H(29)	119.8
C(30)-C(29)-H(29)	119.8
C(29)-C(30)-C(25)	119.9(2)
C(29)-C(30)-H(30)	120.0
C(25)-C(30)-H(30)	120.0
C(8)-C(31)-C(32)	120.0(2)

C(8)-C(31)-H(31)	120.0
C(32)-C(31)-H(31)	120.0
C(5)-C(32)-C(31)	119.80(19)
C(5)-C(32)-H(32)	120.1
C(31)-C(32)-H(32)	120.1
C(1)-C(33)-C(34)	120.4(2)
C(1)-C(33)-H(33)	119.8
C(34)-C(33)-H(33)	119.8
C(33)-C(34)-C(4)	119.8(2)
C(33)-C(34)-H(34)	120.1
C(4)-C(34)-H(34)	120.1
C(36)-C(35)-C(12)	120.1(2)
C(36)-C(35)-H(35)	119.9
C(12)-C(35)-H(35)	119.9
C(35)-C(36)-C(9)	120.0(2)
C(35)-C(36)-H(36)	120.0
C(9)-C(36)-H(36)	120.0
N(2)-N(1)-Sb(1)	118.72(16)
N(3)-N(2)-N(1)	175.0(3)
N(5)-N(4)-Sb(1)	121.84(16)
N(6)-N(5)-N(4)	177.4(2)
N(8)-N(7)-Sb(1)	120.68(15)
N(9)-N(8)-N(7)	174.8(2)
N(11)-N(10)-Sb(1)	120.89(16)
N(12)-N(11)-N(10)	177.2(2)
P(1)-N(13)-P(2)	141.19(12)
N(13)-P(1)-C(13)	105.95(9)
N(13)-P(1)-C(12)	112.91(10)
C(13)-P(1)-C(12)	108.64(9)
N(13)-P(1)-C(4)	112.79(9)
C(13)-P(1)-C(4)	107.38(9)
C(12)-P(1)-C(4)	108.91(9)
N(13)-P(2)-C(5)	108.22(9)
N(13)-P(2)-C(19)	108.78(9)
C(5)-P(2)-C(19)	108.21(9)
N(13)-P(2)-C(25)	114.36(9)

C(5)-P(2)-C(25)	108.75(9)
C(19)-P(2)-C(25)	108.37(9)
N(7)-Sb(1)-N(1)	93.22(8)
N(7)-Sb(1)-N(4)	82.14(7)
N(1)-Sb(1)-N(4)	87.10(9)
N(7)-Sb(1)-N(10)	83.03(8)
N(1)-Sb(1)-N(10)	80.84(9)
N(4)-Sb(1)-N(10)	160.29(8)

Table S24. Anisotropic displacement parameters ($Å^2$x 10^3) for [PNP][$Sb(N_3)_4$]. 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}
C(1)	30(1)	18(1)	13(1)	0(1)	0(1)	-3(1)
C(2)	21(1)	24(1)	20(1)	4(1)	-2(1)	1(1)
C(3)	19(1)	18(1)	17(1)	2(1)	0(1)	4(1)
C(4)	18(1)	9(1)	13(1)	2(1)	2(1)	3(1)
C(5)	17(1)	12(1)	13(1)	3(1)	2(1)	4(1)
C(6)	18(1)	20(1)	17(1)	1(1)	3(1)	3(1)
C(7)	25(1)	21(1)	17(1)	-4(1)	5(1)	1(1)
C(8)	23(1)	17(1)	18(1)	0(1)	0(1)	-1(1)
C(9)	24(1)	45(2)	24(1)	18(1)	7(1)	19(1)
C(10)	31(1)	29(1)	27(1)	12(1)	9(1)	17(1)
C(11)	20(1)	20(1)	19(1)	5(1)	3(1)	6(1)
C(12)	14(1)	19(1)	14(1)	6(1)	4(1)	4(1)
C(13)	13(1)	17(1)	14(1)	-2(1)	0(1)	4(1)
C(14)	19(1)	20(1)	25(1)	-2(1)	0(1)	5(1)
C(15)	22(1)	32(1)	29(1)	-8(1)	-2(1)	14(1)
C(16)	16(1)	49(2)	17(1)	-6(1)	1(1)	9(1)
C(17)	19(1)	42(2)	18(1)	4(1)	4(1)	1(1)
C(18)	21(1)	25(1)	18(1)	4(1)	4(1)	5(1)
C(19)	17(1)	12(1)	14(1)	2(1)	2(1)	5(1)
C(20)	23(1)	17(1)	20(1)	3(1)	0(1)	1(1)
C(21)	34(1)	16(1)	25(1)	6(1)	5(1)	4(1)
C(22)	31(1)	23(1)	16(1)	8(1)	8(1)	14(1)
C(23)	23(1)	26(1)	15(1)	4(1)	2(1)	11(1)
C(24)	19(1)	18(1)	19(1)	2(1)	0(1)	5(1)
C(25)	14(1)	12(1)	16(1)	0(1)	1(1)	1(1)
C(26)	19(1)	17(1)	17(1)	2(1)	0(1)	4(1)
C(27)	21(1)	19(1)	26(1)	3(1)	1(1)	8(1)
C(28)	24(1)	20(1)	30(1)	-4(1)	8(1)	8(1)
C(29)	34(1)	24(1)	17(1)	0(1)	7(1)	9(1)
C(30)	24(1)	16(1)	15(1)	3(1)	4(1)	5(1)
C(31)	16(1)	18(1)	22(1)	2(1)	0(1)	0(1)

C(32)	18(1)	14(1)	16(1)	2(1)	3(1)	4(1)
C(33)	29(1)	15(1)	17(1)	0(1)	8(1)	3(1)
C(34)	19(1)	14(1)	19(1)	2(1)	3(1)	3(1)
C(35)	18(1)	24(1)	16(1)	2(1)	3(1)	3(1)
C(36)	20(1)	43(2)	15(1)	7(1)	0(1)	8(1)
N(1)	28(1)	23(1)	42(1)	-2(1)	13(1)	-4(1)
N(2)	22(1)	20(1)	34(1)	6(1)	-1(1)	-3(1)
N(3)	32(1)	23(1)	100(2)	0(1)	10(1)	4(1)
N(4)	32(1)	42(1)	21(1)	5(1)	5(1)	22(1)
N(5)	22(1)	18(1)	24(1)	-2(1)	-2(1)	8(1)
N(6)	38(1)	34(1)	21(1)	2(1)	0(1)	14(1)
N(7)	24(1)	27(1)	20(1)	2(1)	3(1)	10(1)
N(8)	27(1)	16(1)	24(1)	3(1)	4(1)	4(1)
N(9)	27(1)	30(1)	36(1)	3(1)	8(1)	11(1)
N(10)	23(1)	51(1)	30(1)	15(1)	5(1)	13(1)
N(11)	17(1)	22(1)	29(1)	-2(1)	-2(1)	6(1)
N(12)	32(1)	30(1)	23(1)	-3(1)	-9(1)	15(1)
N(13)	15(1)	14(1)	19(1)	2(1)	3(1)	2(1)
P(1)	13(1)	12(1)	13(1)	1(1)	1(1)	3(1)
P(2)	14(1)	12(1)	13(1)	1(1)	0(1)	3(1)
Sb(1)	18(1)	18(1)	17(1)	3(1)	2(1)	1(1)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [PNP][$Sb(N_3)_4$].

	x	y	z	U(eq)
H(1)	7185	2085	4712	25
H(2)	5721	3001	5457	27
H(3)	6345	3804	6811	21
H(6)	10235	7614	9024	22
H(7)	11475	8861	10148	26
H(8)	13768	9364	10203	24
H(9)	11775	1464	9606	34
H(10)	10411	428	8467	32
H(11)	9091	1569	7721	23
H(14)	7206	6191	8023	26
H(15)	5262	6352	8605	33
H(16)	4201	4658	9239	33
H(17)	5118	2828	9372	32
H(18)	7069	2647	8794	25
H(20)	11919	9026	7138	24
H(21)	11164	10452	6298	29
H(22)	9120	9831	5523	26
H(23)	7860	7788	5554	25
H(24)	8574	6366	6411	22
H(26)	12398	4688	8013	21
H(27)	13441	3211	7330	26
H(28)	13478	3159	5934	29
H(29)	12489	4587	5225	29
H(30)	11402	6036	5897	22
H(31)	14834	8667	9123	23
H(32)	13599	7486	7968	19
H(33)	9324	2132	5277	24
H(34)	9983	2966	6622	20
H(35)	10535	4799	9267	23
H(36)	11815	3637	10019	31

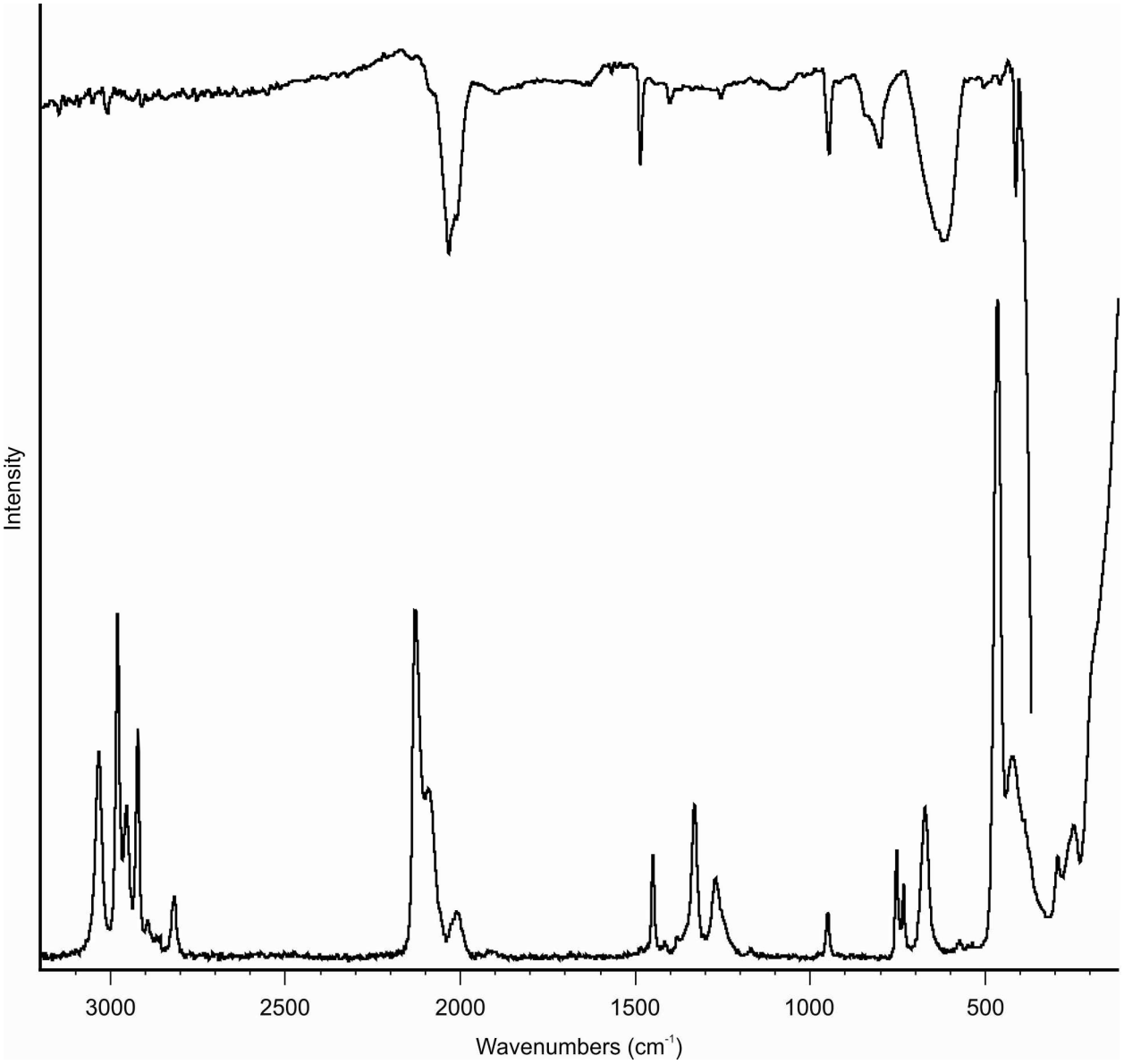

Figure S16: IR (upper trace) and Raman (lower trace) spectra of $[NMe_4][As(N_3)_4]$.

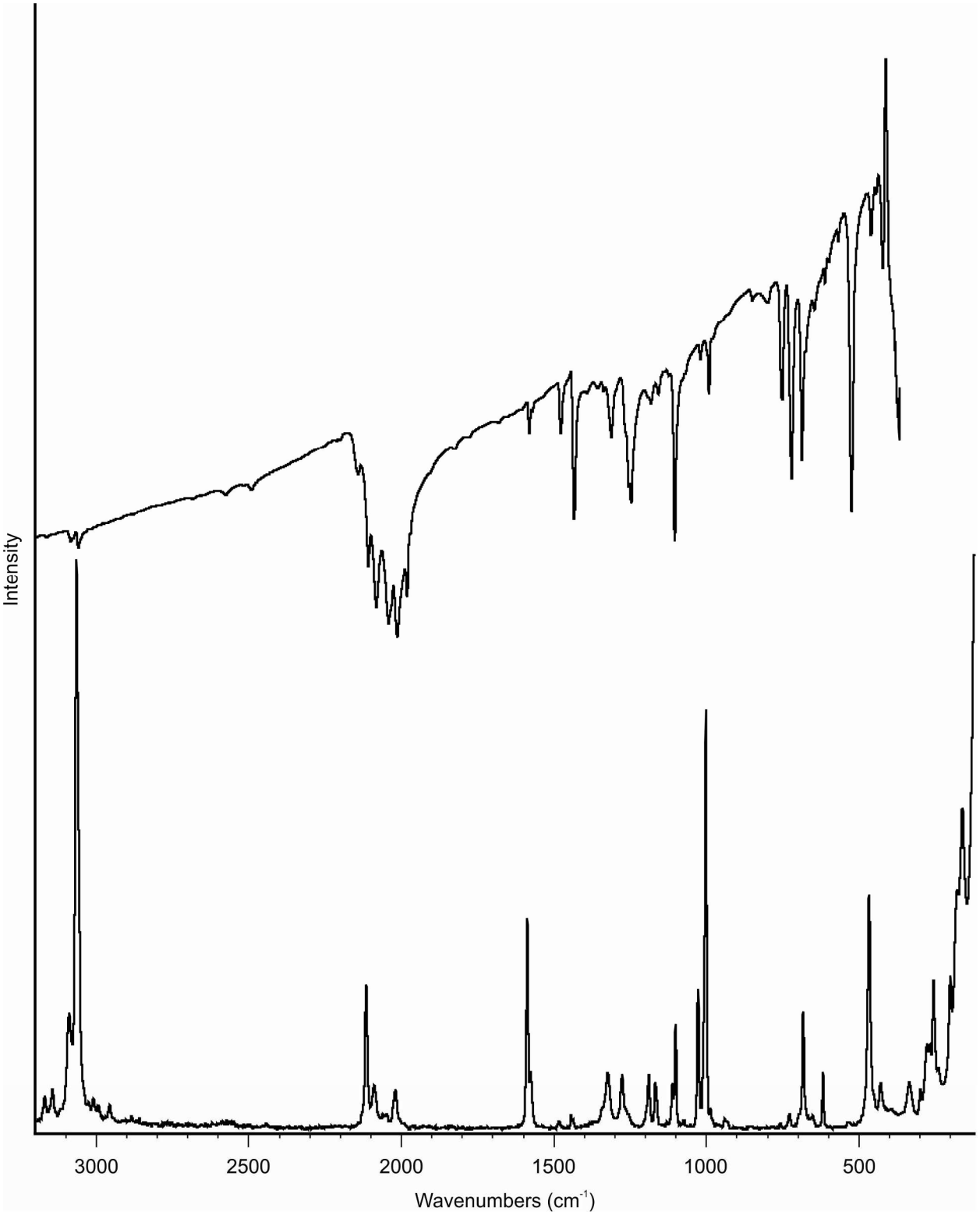

Figure S17: IR (upper trace) and Raman (lower trace) spectra of $[PPh_4][As(N_3)_4]$.

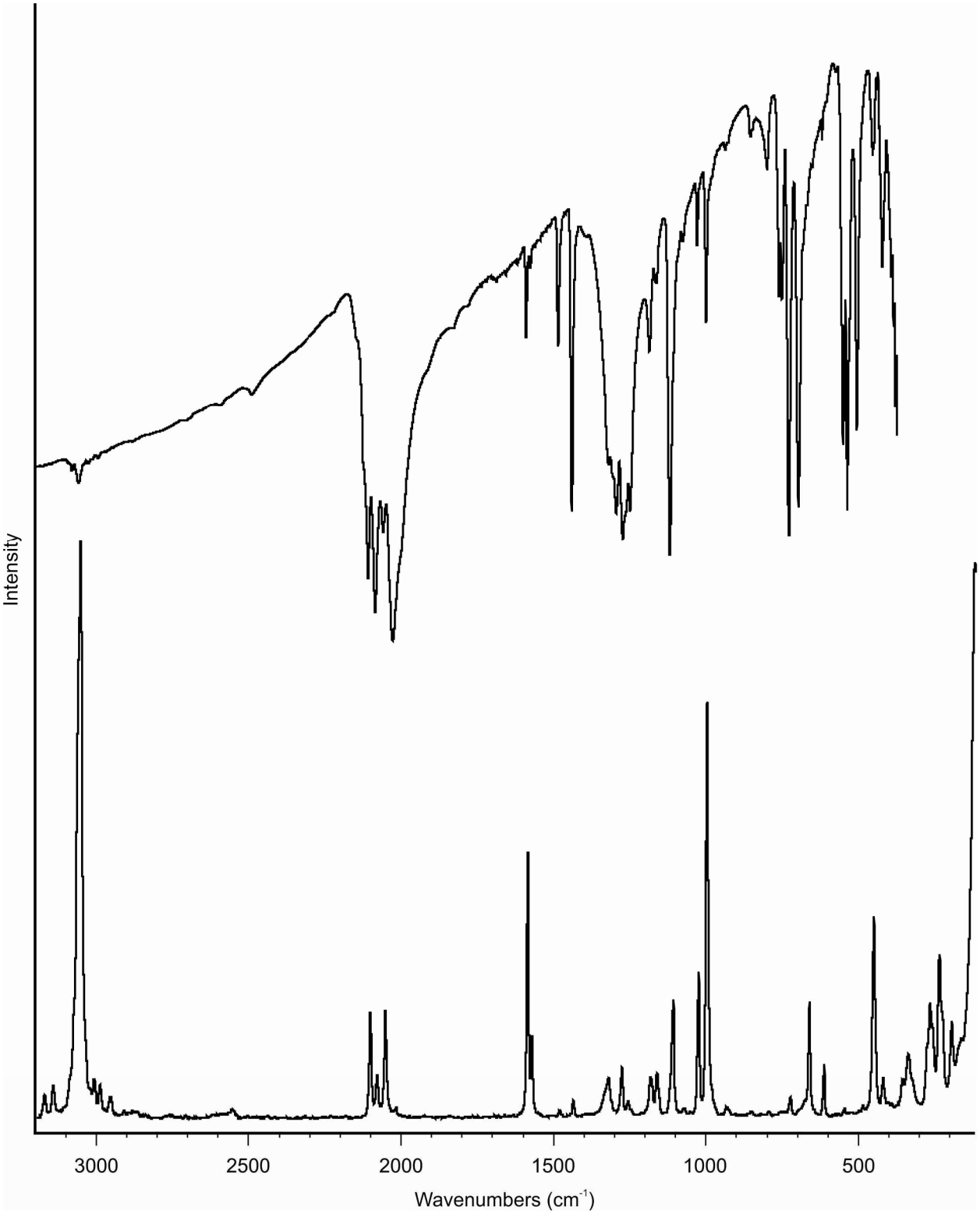

Figure S18: IR (upper trace) and Raman (lower trace) spectra of [PNP][$As(N_3)_4$].

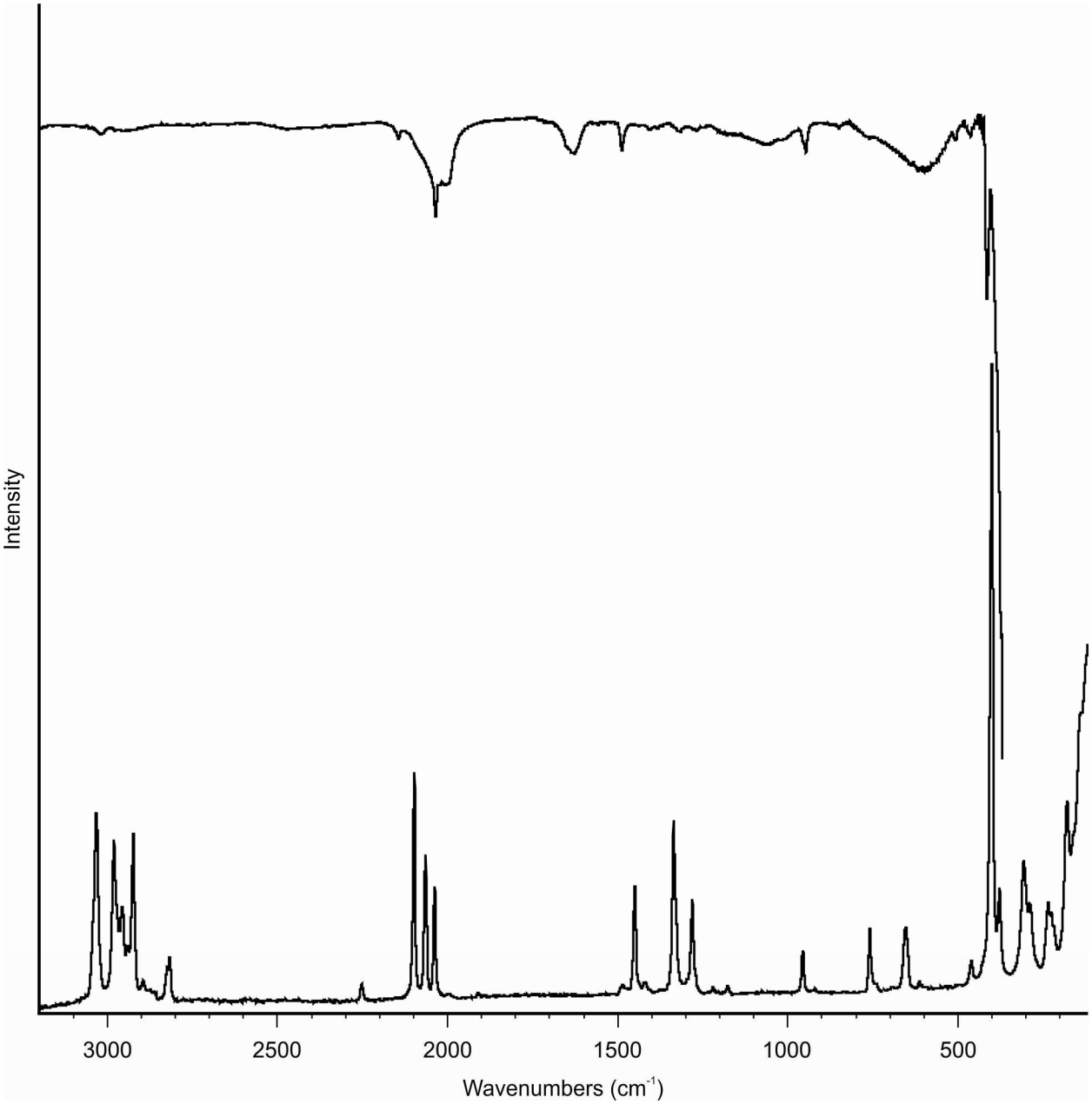

Figure S19: IR (upper trace) and Raman (lower trace) spectra of $[NMe_4][Sb(N_3)_4]$.

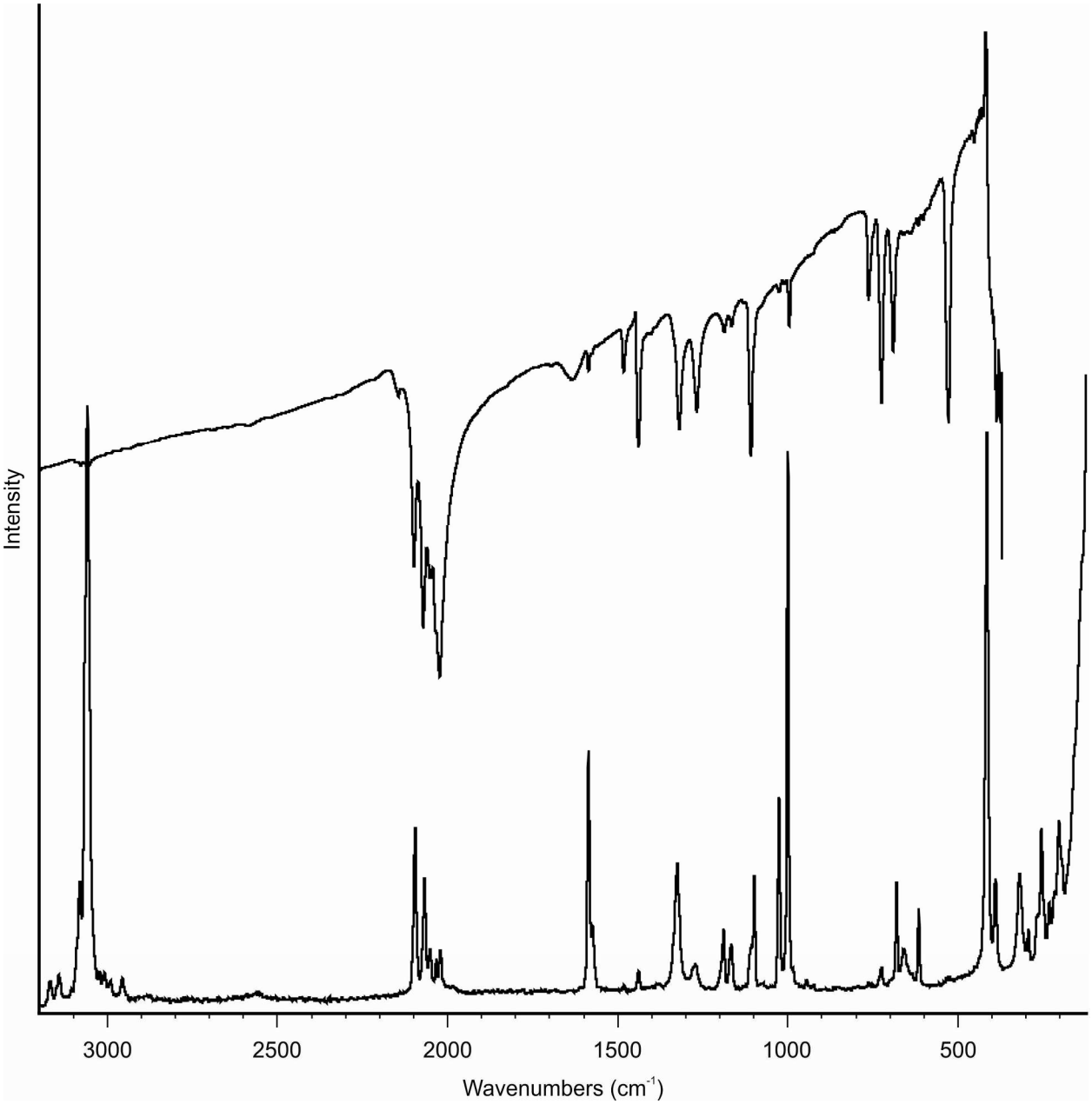

Figure S20: IR (upper trace) and Raman (lower trace) spectra of $[PPh_4][Sb(N_3)_4]$.

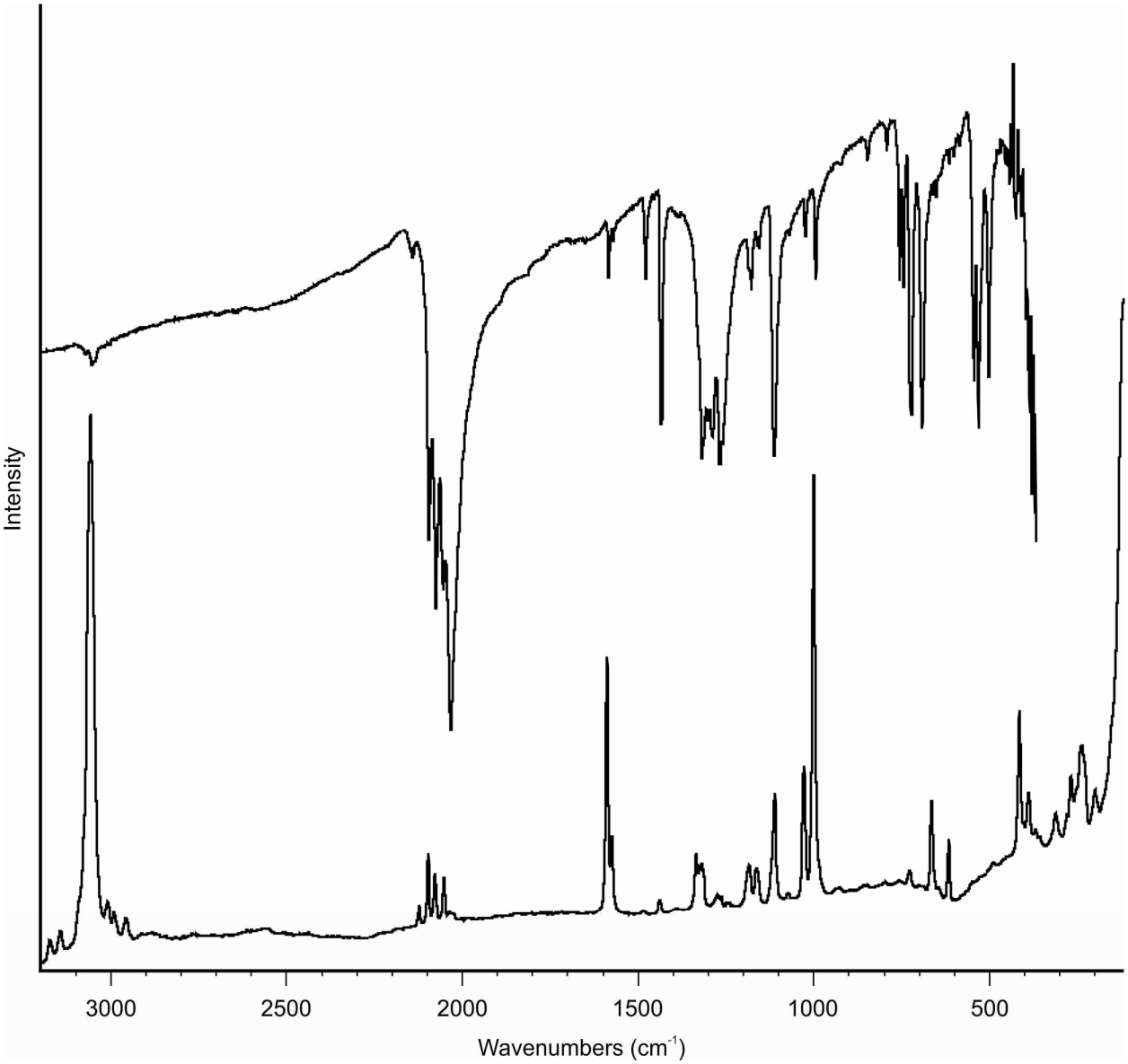

Figure S21: IR (upper trace) and Raman (lower trace) spectra of [PNP][$Sb(N_3)_4$].

Table S26: XYZ-coordinates and SCF energies for all gas-phase M06-2X optimized structures.

$As(N_3)_4^-$ - Conformer #1. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.538671 Hartree

E(SMD-PCM): -989.589153982 Hartree

N	0.114511	2.100205	0.177903
N	0.204859	2.665289	1.232037
N	-0.114511	-2.100205	0.177903
N	-0.204859	-2.665289	1.232037
N	1.432722	-0.162101	-0.866431
N	1.794636	0.819914	-1.488427
N	-1.432722	0.162101	-0.866431
N	-1.794636	-0.819914	-1.488427
N	2.194503	1.668159	-2.105085
N	-2.194503	-1.668159	-2.105085
N	0.285930	3.219975	2.222323
N	-0.285930	-3.219975	2.222323
As	0.000000	0.000000	0.367363

$As(N_3)_4^-$ - Conformer #2. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.540521 Hartree

E(SMD-PCM): -989.591179954 Hartree

As	-0.038424	-0.032834	-0.219767
N	0.125024	-0.144418	1.679029
N	0.942784	0.535756	2.269484

N	1.675398	1.112305	2.895017
N	1.095739	1.833104	-0.096477
N	1.982108	1.868968	-0.898825
N	2.828691	1.911092	-1.661703
N	-1.610231	1.034856	-0.300818
N	-1.588474	2.148619	0.188908
N	-1.650751	3.181227	0.624028
N	-1.271337	-1.642219	-0.089735
N	-2.171449	-1.567885	0.711112
N	-3.024756	-1.523868	1.452302

$As(N_3)_4^-$ - Conformer #3. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.539032 Hartree

E(SMD-PCM): -989.590082966 Hartree

N	-0.085773	-1.295698	0.936784
N	0.989885	-1.795441	1.246265
N	1.946334	-2.307173	1.616650
N	-2.181178	0.319474	0.002743
N	-3.027312	-0.502294	-0.272600
N	-3.869669	-1.256750	-0.527746
N	0.328314	1.569313	0.065636
N	-0.421485	2.197463	0.804787
N	-1.032245	2.867685	1.501830
N	1.867379	-0.453704	-1.090515
N	2.746775	0.315458	-0.756951

N	3.619958	1.020642	-0.482529
As	-0.186875	-0.144025	-0.645772

$As(N_3)_4^-$ - Conformer #4. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.538447 Hartree

E(SMD-PCM): -989.589320262 Hartree

N	-2.235197	0.879276	-0.155770
N	-3.079630	0.030668	-0.266893
N	1.770599	-0.349089	-0.279316
N	2.192180	-0.861419	-1.276436
N	-0.595686	-0.779544	1.210652
N	0.223688	-1.609236	1.558699
N	0.128879	1.885741	0.252745
N	1.282825	2.148698	0.534454
N	0.923269	-2.394800	1.951925
N	2.312152	2.489978	0.823897
N	-3.900223	-0.748343	-0.369375
N	2.603257	-1.348472	-2.220471
As	-0.327290	0.180526	-0.419319

$As(N_3)_4^-$ - Conformer #5. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.538485 Hartree

E(SMD-PCM): -989.590457520 Hartree

N	-0.061139	2.099571	0.889856
N	-0.720377	2.672047	0.062476

N	0.061139	-2.099571	0.889856
N	0.720377	-2.672047	0.062476
N	1.475417	-0.034563	-0.197602
N	1.767617	0.977888	-0.803222
N	-1.475417	0.034563	-0.197602
N	-1.767617	-0.977888	-0.803222
N	2.093875	1.874397	-1.395713
N	-2.093875	-1.874397	-1.395713
N	-1.341094	3.243413	-0.696133
N	1.341094	-3.243413	-0.696133
As	0.000000	0.000000	1.017040

$As(N_3)_4^-$ - Conformer #6. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.534721 Hartree

E(SMD-PCM): -989.588348789 Hartree

N	-0.154351	0.146850	-0.102261
N	-0.183495	0.697653	0.982642
N	-0.128560	1.215581	1.978482
N	-0.781329	-0.156926	-2.709145
N	-0.331183	0.935885	-2.926791
N	0.102243	1.960614	-3.157333
N	-1.580159	-2.140539	-1.222521
N	-2.284823	-2.925256	-0.615761
N	-2.896142	-3.720885	-0.110393

N	-2.653836	-0.697795	1.013880
N	-1.984193	-1.366942	1.754993
N	-1.349834	-1.996953	2.458427
As	-1.823613	-0.278127	-0.944305

$As(N_3)_4^-$ - Conformer #7. M06-2X/(cc-pwCVTZ-PP on As, cc-pVTZ on N)

E(SCF): -989.535948 Hartree

E(SMD-PCM): -989.589660684 Hartree

N	0.005657	-0.025645	-0.042193
N	0.021420	-0.046281	1.172634
N	0.120404	-0.058699	2.292437
N	-0.584850	0.964066	-2.469257
N	0.385132	0.353396	-2.847333
N	1.300966	-0.188060	-3.230792
N	-1.625147	-1.452331	-1.924096
N	-2.512386	-2.264437	-1.751324
N	-3.304004	-3.057375	-1.659388
N	-2.639826	-0.866988	0.699910
N	-2.145842	-1.902071	1.057360
N	-1.678249	-2.882919	1.396571
As	-1.668654	0.192288	-0.944920

$Sb(N_3)_4^-$ - Conformer #1. M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.106234 Hartree

E(SMD-PCM): -897.156151984 Hartree

N	-2.117450	0.533779	-0.314075
N	-2.879150	0.096835	-1.130843
N	2.168855	-0.407587	0.054453
N	2.709359	-1.418494	-0.296189
N	-0.245435	-0.718284	1.578941
N	-1.304767	-0.567880	2.150249
N	0.377925	1.841718	-0.144290
N	1.467814	2.250294	0.198017
N	-2.251888	-0.462958	2.748332
N	2.443555	2.714716	0.509147
N	-3.622642	-0.297639	-1.896493
N	3.249678	-2.365352	-0.621381
Sb	-0.000247	-0.171470	-0.410452

$Sb(N_3)_4^-$ - Conformer #2 M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.108400 Hartree

E(SMD-PCM): -897.158718855 Hartree

N	-0.223262	-0.007641	-0.011295
N	-0.231904	-0.046251	1.200209
N	-0.159158	-0.064526	2.322896
N	-2.955833	-0.634534	0.841438
N	-3.953314	-0.023792	1.100425
N	-4.902352	0.546205	1.365204

N	-1.957921	-2.275466	-1.371384
N	-2.499832	-3.015220	-0.578678
N	-2.983643	-3.764788	0.106982
N	-0.562402	-0.273137	-2.812964
N	0.381282	-1.022040	-2.767726
N	1.279093	-1.710364	-2.764977
Sb	-1.957477	-0.204722	-1.147967

$Sb(N_3)_4^-$ - Conformer #3 M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.107345 Hartree

E(SMD-PCM): -897.158100244 Hartree

N	-0.001860	-1.344209	0.816318
N	1.051871	-1.866491	1.106703
N	2.000154	-2.381209	1.430623
N	-2.181045	0.300493	0.008278
N	-2.908218	-0.634497	0.196115
N	-3.624591	-1.498086	0.377396
N	0.256479	1.792918	-0.004864
N	-0.512791	2.360003	0.741335
N	-1.170114	2.947651	1.438873
N	2.047037	-0.177358	-0.999680
N	2.778683	0.423063	-0.254406
N	3.497216	0.978289	0.422376
Sb	-0.153837	-0.063147	-0.837088

$Sb(N_3)_4^-$ - Conformer #4. M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.106093 Hartree

E(SMD-PCM): -897.156767045 Hartree

N	-2.333055	0.816365	-0.015196
N	-3.213364	0.003217	-0.095844
N	1.884787	-0.339871	-0.197776
N	2.551182	-0.561974	-1.169469
N	-0.621823	-1.196964	1.027433
N	0.234407	-1.980138	1.378943
N	0.139136	1.891150	0.566733
N	1.281066	2.200430	0.832239
N	0.975031	-2.737819	1.757919
N	2.308926	2.560276	1.115619
N	-4.075022	-0.734159	-0.164810
N	3.200974	-0.776861	-2.078087
Sb	-0.293191	0.172268	-0.505856

$Sb(N_3)_4^-$ - Conformer #5 M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.107842 Hartree

E(SMD-PCM): -897.159606469 Hartree

N	0.468462	2.137970	0.671551
N	0.058555	2.781071	-0.259640
N	-0.468462	-2.137970	0.671551
N	-0.058555	-2.781071	-0.259640
N	1.562780	-0.426449	-0.327851

N	2.191936	0.459049	-0.863429
N	-1.562780	0.426449	-0.327851
N	-2.191936	-0.459049	-0.863429
N	2.814531	1.235181	-1.390535
N	-2.814531	-1.235181	-1.390535
N	-0.315456	3.423299	-1.114548
N	0.315456	-3.423299	-1.114548
Sb	0.000000	0.000000	0.997248

$Sb(N_3)_4^-$ - Conformer #6 M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.103963 Hartree

E(SMD-PCM): -897.156962295 Hartree

N	-0.213673	0.410526	-0.095267
N	-0.152325	0.794136	1.052789
N	-0.030051	1.165812	2.109298
N	-0.901452	-0.038699	-2.793352
N	-0.239028	0.939336	-3.008682
N	0.395901	1.848454	-3.254518
N	-1.787965	-2.175017	-1.311239
N	-2.383893	-3.003455	-0.657039
N	-2.909696	-3.827860	-0.097442
N	-2.637740	-0.752217	1.145513
N	-1.905309	-1.447040	1.803292
N	-1.228331	-2.098670	2.438197
Sb	-2.055712	-0.142145	-0.931638

$Sb(N_3)_4^-$ - Conformer #7 M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -897.105491 Hartree

E(SMD-PCM): -897.158334927 Hartree

N	0.007633	-0.044159	-0.004963
N	0.001758	-0.073972	1.205959
N	0.065907	-0.095689	2.330878
N	-0.402646	0.608405	-2.724371
N	0.506550	-0.142712	-2.970999
N	1.373511	-0.818667	-3.239286
N	-1.879048	-1.682291	-1.976377
N	-2.751010	-2.465360	-1.670261
N	-3.543461	-3.233396	-1.441890
N	-2.799467	-0.732856	0.685211
N	-2.393254	-1.764876	1.155663
N	-2.025679	-2.735815	1.612610
Sb	-1.772191	0.210182	-1.082056

$[Sb(N_3)_4]_2^-$ - [Sb-2 – Sb-3]. M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -1794.165127 Hartree

E(SMD-PCM): -1794.33065468 Hartree

N	0.137657	-0.220733	-0.004955
N	0.131346	-0.122488	1.118451

N	0.213360	-0.014707	2.318037
Sb	-1.454513	0.009797	3.584856
N	-2.004728	-1.978100	3.223332
N	-1.775447	-2.844926	4.032222
N	-1.594694	-3.706229	4.739201
N	0.038055	-0.819257	5.067104
N	0.977254	-1.481029	4.724655
N	1.881809	-2.106622	4.434926
N	-2.556708	0.362625	1.662778
N	-3.640296	0.851224	1.635617
N	-4.679430	1.317037	1.555466
N	-4.472285	-0.016387	4.473490
N	-5.136055	0.909609	4.530288
N	-5.828664	1.874271	4.638296
Sb	-7.004936	2.805580	2.939144
N	-8.018538	3.738471	4.523114
N	-7.620101	3.742406	5.663088
N	-7.317774	3.791624	6.748446
N	-5.434438	4.171716	2.827664
N	-4.325607	3.812107	3.156018
N	-3.272320	3.535672	3.443392
N	-8.081571	4.334738	1.736751
N	-8.093088	5.483750	2.082192
N	-8.132288	6.580046	2.376911

$[Sb(N_3)_4]_2^-$ - $[Sb\text{-}3]_2$. M06-2X/(cc-pwCVTZ-PP on Sb, cc-pVTZ on N)

E(SCF): -1794.164050 Hartree

E(SMD-PCM): -1794.32670427 Hartree

N	0.080573	0.029646	0.029496
N	0.071881	-0.026848	1.155575
N	0.146378	-0.092615	2.359242
Sb	-1.538057	-0.072160	3.611401
N	-2.423533	-1.873882	3.017755
N	-2.235410	-2.903326	3.622691
N	-2.101101	-3.898069	4.136551
N	-0.186162	-1.337421	4.923384
N	0.700445	-2.013731	4.484247
N	1.555774	-2.659340	4.102411
N	-2.551190	0.697327	1.801631
N	-3.687705	0.437833	1.539152
N	-4.763049	0.215015	1.244368
N	-4.589053	0.440460	4.437396
N	-5.664459	0.217402	4.143022
N	-6.801020	-0.042295	3.880827
Sb	-7.814310	0.727322	2.071117
N	-9.498643	0.747273	3.323419
N	-9.423912	0.682105	4.527112
N	-9.432348	0.626103	5.653207
N	-6.929365	2.529114	2.665353
N	-7.116214	3.558360	2.059710

N	-7.249465	4.552911	1.545207
N	-9.166355	1.992762	0.759406
N	-10.051586	2.670005	1.199947
N	-10.905594	3.316498	1.583225

Table S27: Unscaled azide stretching Raman frequencies, calculated at several levels of theory.

	$As(N_3)_4^-$				$Sb(N_3)_4^-$		
	B3LYP/ cc-pwCVDZ	PCM*	M06-2X cc-pwCVTZ	PCM*	B3LYP/ cc-pwCVDZ	PCM*	M06-2X cc-pwCVTZ
1	2247	2233	2320	2302	2241	2220	2312
	2224	2199	2293	2268	2221	2192	2287
	2201	2173	2258	2226	2206	2175	2259
	2172	2134	2220	2181	2183	2144	2231
2	-	2232	2324	2302	-	2218	2316
	-	2199	2289	2265	-	2189	2283
	-	2181	2265	2216	-	2180	2270
	-	2149	2231	2172	-	2157	2240
3	-	2234	2322	-	-	2220	2313
	-	2199	2293	-	-	2192	2289
	-	2175	2249	-	-	2176	2260
	-	2149	2231	-	-	2158	2248
4	2249	2233	2321	-	2242	2221	2313
	2219	2198	2287	-	2216	2192	2282
	2203	2176	2257	-	2205	2175	2261
	2176	2137	2223	-	2183	2145	2236
5	2246	2232	2319	-	2239	2219	2311
	2226	2201	2295	-	2221	2192	2289
	2207	2177	2253	-	2211	2181	2263
	2193	2157	2237	-	2201	2168	2252
6	-	-	2315	-	-	-	2307
	-	-	2282	-	-	-	2272
	-	-	2246	-	-	-	2253
	-	-	2214	-	-	-	2233
7	-	-	2317	-	-	-	2308
	-	-	2285	-	-	-	2272
	-	-	2264	-	-	-	2268
	-	-	2216	-	-	-	2233
[2-3]	-	-	-	-	-	2221	2314
	-	-	-	-	-	2216	2303
	-	-	-	-	-	2192	2281
	-	-	-	-	-	2192	2276
	-	-	-	-	-	2184	2259
	-	-	-	-	-	2178	2246
	-	-	-	-	-	2134	2233
	-	-	-	-	-	2115	2223

[3-3]	-	-	-	-	-	-	2306
	-	-	-	-	-	-	2281
	-	-	-	-	-	-	2245
	-	-	-	-	-	-	2236

*Acetone

Table S28: Unscaled M06-2X/cc-pwCVTZ gas-phase frequencies for $As(N_3)_4^-$ conformers 1-7, with corresponding IR and Raman intensities.

As1	Mode	Freq (cm^{-1})	Raman int	IR int
	1	16.2	7.0	2.7
	2	20.5	4.4	0.0
	3	27.2	13.3	0.1
	4	31.8	1.5	0.3
	5	60.3	9.0	1.1
	6	102.7	2.9	3.2
	7	141.9	9.3	1.5
	8	149.4	5.9	5.4
	9	181.0	11.3	1.2
	10	185.8	0.3	3.3
	11	237.6	2.1	0.9
	12	261.9	2.3	128.3
	13	283.9	2.3	42.0
	14	294.9	3.6	367.4
	15	359.5	3.8	2.6
	16	448.7	2.9	118.2
	17	490.6	28.9	39.8
	18	648.0	0.1	9.9
	19	651.0	0.9	11.4
	20	677.2	1.1	0.1
	21	677.4	0.7	16.5
	22	719.7	1.9	18.0
	23	726.1	0.4	8.9
	24	734.6	3.0	51.9
	25	735.0	8.9	7.3
	26	1359.8	6.2	397.7
	27	1373.1	7.7	228.2
	28	1403.1	19.1	197.0
	29	1412.4	55.0	70.3
	30	2220.1	55.5	1875.9
	31	2257.5	29.7	1722.3
	32	2292.9	77.3	1283.0
	33	2320.3	172.9	294.6

As2	Mode	Freq (cm^{-1})	Raman int	IR int
	1	24.3	5.6	0.9
	2	26.0	6.5	1.4

3	36.8	10.2	0.2
4	56.6	4.8	0.2
5	67.2	0.5	2.3
6	90.5	15.2	1.0
7	146.5	5.6	2.0
8	158.4	3.3	2.4
9	183.9	1.9	26.7
10	203.0	0.1	7.5
11	257.8	4.8	8.8
12	265.7	1.9	233.1
13	288.4	4.3	64.8
14	299.5	4.5	144.3
15	360.8	10.6	90.3
16	438.0	3.4	97.1
17	482.9	30.0	27.1
18	646.5	0.4	10.2
19	649.4	0.9	6.8
20	679.4	0.4	11.4
21	685.2	0.9	8.7
22	718.2	1.3	10.0
23	726.6	6.1	39.5
24	731.8	8.9	36.8
25	736.1	4.5	18.7
26	1361.4	3.3	191.8
27	1372.2	12.6	332.0
28	1381.0	16.6	224.1
29	1417.7	43.2	111.0
30	2230.8	8.5	2427.2
31	2264.7	134.7	420.1
32	2288.6	70.0	686.1
33	2324.3	97.4	936.8

As3	Mode	Freq (cm^{-1})	Raman int	IR int
	1	18.0	5.9	1.2
	2	30.8	7.9	0.5
	3	41.1	6.2	0.2
	4	50.9	6.1	0.5
	5	70.7	2.7	2.9
	6	93.7	8.2	0.5
	7	148.1	4.7	10.6
	8	153.7	4.5	1.8

9	180.5	2.5	9.1
10	205.8	3.0	27.3
11	247.5	2.9	2.6
12	278.2	3.5	450.2
13	285.5	4.6	28.8
14	300.2	3.2	29.3
15	339.0	5.8	8.1
16	439.4	8.7	103.1
17	484.8	25.1	32.2
18	647.0	0.4	10.3
19	652.5	0.8	8.2
20	679.5	1.3	2.0
21	680.1	0.4	18.4
22	721.9	4.7	27.7
23	724.9	3.9	17.7
24	726.6	5.7	13.0
25	736.7	4.1	28.4
26	1360.0	3.5	330.9
27	1371.8	8.9	128.0
28	1384.0	19.6	331.7
29	1411.6	47.8	108.8
30	2230.9	11.6	2493.1
31	2249.1	113.8	107.8
32	2292.7	81.9	1335.8
33	2321.9	125.9	564.7

As4	Mode	Freq (cm^{-1})	Raman int	IR int
	1	19.7	13.5	0.9
	2	25.3	1.2	0.7
	3	28.5	9.2	0.9
	4	50.2	4.1	0.5
	5	66.8	10.8	0.9
	6	93.5	2.8	2.3
	7	145.0	3.9	0.7
	8	156.6	7.4	2.7
	9	177.3	3.1	8.6
	10	206.0	3.7	6.5
	11	251.5	4.7	9.2
	12	257.6	3.1	134.6

13	273.3	4.8	39.3
14	302.2	3.7	254.0
15	364.2	4.5	81.1
16	446.3	6.5	105.4
17	485.2	25.3	41.4
18	647.5	0.4	6.8
19	652.1	1.1	7.3
20	674.6	1.4	10.7
21	682.4	0.9	6.9
22	715.3	1.1	15.9
23	726.0	3.2	20.3
24	732.2	4.3	6.6
25	736.6	7.3	58.7
26	1360.2	4.3	261.7
27	1378.6	2.0	363.9
28	1397.5	33.5	121.8
29	1414.7	40.7	103.0
30	2223.1	55.2	2172.7
31	2256.7	48.5	1128.4
32	2286.7	89.5	943.7
33	2321.2	129.1	700.6

As5	Mode	Freq (cm^{-1})	Raman int	IR int
	1	31.9	0.0	0.0
	2	32.2	6.4	0.4
	3	51.3	14.2	0.2
	4	58.8	1.7	1.2
	5	85.7	10.9	0.7
	6	101.7	2.7	3.0
	7	163.3	2.2	38.4
	8	163.4	1.8	0.6
	9	180.4	5.6	0.1
	10	207.8	2.7	31.5
	11	240.0	1.7	0.0
	12	266.3	3.7	407.4
	13	293.0	1.2	23.7
	14	307.9	3.0	20.4
	15	323.4	5.8	0.8

16	440.0	4.1	122.2
17	476.8	28.3	19.2
18	650.6	0.3	8.3
19	653.0	0.7	8.3
20	676.4	0.8	7.4
21	676.7	0.2	10.5
22	719.9	0.5	44.3
23	720.4	14.1	5.6
24	726.6	5.5	2.4
25	727.3	2.3	34.2
26	1366.6	3.3	340.3
27	1376.1	8.7	45.0
28	1386.9	5.3	385.4
29	1400.8	53.7	95.4
30	2237.4	44.2	1614.1
31	2253.2	70.9	232.8
32	2295.1	62.6	1586.4
33	2319.5	136.5	592.5

As6	Mode	Freq (cm^{-1})	Raman int	IR int
	1	31.0	4.6	1.4
	2	42.7	1.6	1.2
	3	57.1	4.7	0.4
	4	77.5	2.7	0.9
	5	85.9	4.9	0.4
	6	88.3	4.8	0.2
	7	119.1	5.5	8.8
	8	156.0	3.5	0.9
	9	171.1	3.7	4.1
	10	209.6	7.3	11.5
	11	249.2	5.0	57.4
	12	263.7	5.1	276.9
	13	266.1	1.2	17.8
	14	301.8	4.0	8.1
	15	353.3	4.7	131.1
	16	448.6	6.3	124.3
	17	480.3	28.5	24.1
	18	646.7	0.3	4.1
	19	649.4	2.6	9.5

20	675.7	1.4	10.1
21	689.5	0.5	9.6
22	718.7	4.1	13.3
23	726.5	3.8	9.2
24	735.0	2.2	11.3
25	737.9	8.0	36.8
26	1357.9	3.8	322.5
27	1370.5	4.5	108.3
28	1381.5	10.4	372.1
29	1400.2	55.5	37.9
30	2214.1	41.9	1149.6
31	2245.8	50.7	1262.9
32	2282.4	74.5	1407.2
33	2315.1	155.1	535.4

As7	Mode	Freq (cm^{-1})	Raman int	IR int
	1	29.2	6.5	0.1
	2	39.7	4.3	0.5
	3	52.5	6.1	0.3
	4	65.3	6.1	0.7
	5	86.9	4.8	0.0
	6	94.0	6.2	0.2
	7	123.5	5.6	9.2
	8	170.4	2.5	11.7
	9	170.6	2.8	3.9
	10	215.6	3.4	10.5
	11	251.9	1.2	148.1
	12	264.2	3.8	159.1
	13	268.1	0.4	5.4
	14	304.8	3.5	19.7
	15	358.4	5.3	118.7
	16	440.9	5.1	134.6
	17	476.3	33.5	8.8
	18	643.9	0.1	4.4
	19	646.8	2.6	10.5
	20	675.8	0.3	13.5
	21	690.7	0.3	11.6
	22	719.5	2.2	19.1
	23	726.2	2.8	16.3

24	729.9	12.5	36.2
25	737.6	3.3	8.7
26	1367.2	4.6	364.5
27	1373.4	6.4	276.8
28	1376.4	7.6	63.1
29	1393.2	41.9	141.5
30	2215.6	40.7	616.5
31	2264.2	60.9	1200.9
32	2284.8	76.6	1397.6
33	2316.9	141.8	639.5

Table S29: Unscaled M06-2X/cc-pwCVTZ gas-phase frequencies for $Sb(N_3)_4^-$ conformers **1**-**7** and dimers **2**-**3** and **3**-**3**, with corresponding IR and Raman intensities.

Sb1	Mode	Freq (cm^{-1})	Raman int	IR int
	1	14.2	8.1	1.8
	2	24.8	5.0	1.4
	3	28.6	12.4	0.2
	4	53.9	9.1	1.8
	5	55.7	4.8	1.4
	6	83.6	2.4	3.2
	7	124.6	6.1	1.9
	8	127.5	5.5	4.9
	9	147.6	7.0	0.5
	10	156.7	1.9	4.8
	11	204.5	1.5	5.2
	12	230.9	2.9	27.7
	13	235.6	4.2	22.9
	14	311.3	0.9	365.3
	15	352.7	4.0	3.5
	16	423.1	5.6	104.6
	17	452.6	35.6	39.0
	18	658.5	0.6	9.6
	19	661.1	1.1	9.0
	20	677.8	1.4	5.4
	21	678.0	0.7	12.0
	22	713.3	1.6	15.3
	23	716.9	3.9	15.3
	24	718.9	5.8	12.6
	25	723.0	7.4	30.3
	26	1380.9	6.0	411.4
	27	1390.8	8.1	226.5
	28	1410.0	24.9	240.3
	29	1419.1	55.1	66.4
	30	2230.9	53.7	2435.0
	31	2259.3	34.1	1309.9
	32	2287.3	65.6	1559.9
	33	2311.8	170.1	263.0

Sb2 (TS)	Mode	Freq (cm^{-1})	Raman int	IR int

1	-8.2	4.8	2.2
2	29.3	11.7	0.4
3	33.5	8.2	0.1
4	53.6	1.3	3.2
5	54.3	1.0	0.0
6	75.2	14.8	0.6
7	133.6	6.6	0.6
8	146.3	2.3	5.8
9	148.0	0.9	6.6
10	172.0	0.0	7.1
11	224.6	1.4	43.5
12	227.5	5.5	6.1
13	240.4	4.8	53.5
14	317.7	0.9	200.4
15	359.4	6.3	97.9
16	414.6	3.7	98.8
17	444.8	36.9	28.3
18	661.3	0.1	7.1
19	663.5	1.2	8.7
20	677.7	1.2	2.4
21	678.2	0.2	18.4
22	711.7	1.4	8.2
23	718.0	3.5	17.5
24	720.2	15.5	50.0
25	723.2	3.9	6.0
26	1383.6	4.4	243.0
27	1388.2	14.0	316.3
28	1397.4	14.8	225.9
29	1418.9	44.8	118.0
30	2240.1	12.4	2290.1
31	2270.4	107.1	550.2
32	2283.2	72.4	867.1
33	2315.6	96.3	1043.8

Sb3	Mode	Freq (cm^{-1})	Raman int	IR int
	1	16.8	6.6	1.7
	2	28.8	6.7	0.2
	3	45.0	6.5	0.1
	4	56.4	3.2	1.2

5	61.7	6.0	2.1
6	74.5	7.1	0.5
7	131.2	2.6	2.6
8	136.3	3.9	4.5
9	149.1	3.3	3.3
10	183.2	3.6	15.3
11	215.8	2.3	4.0
12	238.5	2.5	26.5
13	244.1	2.8	85.2
14	323.4	4.9	252.0
15	337.2	3.2	2.2
16	414.7	7.3	104.0
17	442.8	34.1	28.1
18	659.9	0.6	9.3
19	661.5	1.0	8.5
20	676.7	1.1	8.9
21	678.7	0.6	11.3
22	714.4	9.3	8.7
23	714.9	2.2	32.1
24	717.8	5.9	12.1
25	720.2	4.4	18.4
26	1381.3	5.4	263.4
27	1389.6	10.3	247.7
28	1396.9	14.8	302.7
29	1416.0	46.2	117.1
30	2248.0	19.1	2245.5
31	2259.7	83.4	280.6
32	2289.0	74.2	1573.1
33	2312.5	140.9	614.5

Sb4	Mode	Freq (cm^{-1})	Raman int	IR int
	1	25.7	6.4	2.0
	2	26.6	10.2	1.3
	3	34.1	4.1	0.6
	4	54.3	2.9	0.3
	5	60.0	13.0	1.6
	6	76.7	2.2	3.0
	7	124.6	4.0	1.9
	8	128.6	7.6	0.6

9	151.1	2.1	6.5
10	172.2	3.6	6.9
11	213.8	2.1	21.5
12	225.3	4.2	12.6
13	241.4	4.0	25.7
14	314.8	2.3	273.0
15	358.0	3.1	67.1
16	423.2	4.6	102.4
17	448.2	35.0	36.9
18	659.2	0.3	5.6
19	661.7	1.2	8.7
20	676.2	1.1	11.2
21	679.0	1.0	7.1
22	711.4	1.4	13.4
23	716.3	4.4	10.9
24	720.4	9.8	22.5
25	722.7	3.8	30.5
26	1381.7	5.5	278.5
27	1391.2	3.9	319.5
28	1406.3	27.8	220.2
29	1416.8	51.0	74.2
30	2236.4	46.4	2576.8
31	2261.2	44.8	979.2
32	2281.7	90.2	929.0
33	2312.5	122.9	803.8

Sb5	Mode	Freq (cm^{-1})	Raman int	IR int
	1	25.9	6.3	0.1
	2	36.6	0.3	0.0
	3	45.8	13.2	0.4
	4	53.9	2.6	1.0
	5	67.7	9.2	1.0
	6	89.2	2.4	1.6
	7	137.7	5.2	0.2
	8	142.7	2.5	11.4
	9	149.8	3.9	0.6
	10	181.9	1.8	12.2
	11	214.6	1.3	3.3
	12	242.4	3.5	116.2
	13	242.7	1.8	26.3
	14	322.3	3.9	197.5

15	325.0	2.2	0.0
16	411.8	4.1	110.0
17	437.6	35.5	19.4
18	660.9	0.4	8.5
19	662.3	0.9	7.5
20	676.4	0.9	6.1
21	676.9	0.4	13.4
22	712.8	0.7	41.5
23	713.5	14.2	4.1
24	716.7	5.9	3.3
25	718.3	2.9	21.2
26	1386.3	2.8	335.1
27	1390.5	11.3	8.5
28	1395.7	6.6	371.7
29	1408.5	44.2	159.3
30	2251.9	43.8	1233.5
31	2263.4	49.7	249.4
32	2288.9	61.4	1895.8
33	2311.0	138.3	777.2

Sb6	Mode	Freq (cm^{-1})	Raman int	IR int
	1	18.4	6.4	1.7
	2	47.2	2.5	0.1
	3	49.3	2.1	0.7
	4	68.4	5.0	1.3
	5	72.5	2.5	1.2
	6	82.3	4.0	0.0
	7	108.5	6.7	3.0
	8	118.5	4.1	0.6
	9	148.5	4.0	6.7
	10	189.7	6.5	7.7
	11	213.9	2.4	10.6
	12	238.3	0.8	13.6
	13	247.6	3.5	109.6
	14	309.1	5.4	96.4
	15	349.3	2.1	118.4
	16	417.1	6.7	113.7
	17	444.8	36.3	26.9
	18	659.4	0.3	5.5
	19	661.0	1.9	9.2
	20	673.1	0.9	10.6

21	682.3	0.4	8.0
22	713.3	4.0	16.3
23	717.7	4.3	8.7
24	721.9	3.6	6.0
25	723.9	9.5	28.2
26	1377.3	5.7	288.8
27	1379.0	6.3	82.7
28	1390.8	10.4	401.6
29	1412.5	53.8	81.5
30	2233.2	43.0	713.2
31	2253.7	26.0	1736.4
32	2272.6	84.8	1258.2
33	2307.4	142.5	778.0

Sb7	Mode	Freq (cm^{-1})	Raman int	IR int
	1	23.6	10.6	0.2
	2	34.7	0.4	0.3
	3	43.0	5.3	0.2
	4	56.7	7.5	0.8
	5	80.4	4.6	0.2
	6	86.5	3.3	0.1
	7	109.0	6.3	1.0
	8	141.6	1.9	6.1
	9	147.3	2.1	6.5
	10	194.5	5.1	8.5
	11	220.7	1.5	20.8
	12	239.6	0.3	9.8
	13	246.4	4.6	120.4
	14	302.9	2.1	54.4
	15	359.4	1.9	129.2
	16	413.0	4.9	118.0
	17	442.3	37.4	14.5
	18	656.4	0.2	5.8
	19	658.3	1.7	9.3
	20	676.6	0.4	11.7
	21	682.3	0.3	12.2
	22	713.5	2.5	18.0
	23	720.3	3.1	11.8
	24	721.8	13.3	30.6
	25	725.5	3.0	6.9
	26	1379.9	6.6	35.7

27	1381.9	5.6	330.1
28	1390.0	6.8	323.8
29	1402.8	40.8	151.4
30	2232.6	34.2	332.2
31	2267.6	54.7	1287.4
32	2271.6	75.7	1381.0
33	2308.2	115.0	969.6

Sb2-Sb3	Mode	Freq (cm^{-1})	Raman int	IR int
	1	12.0	1.1	1.2
	2	14.4	0.6	0.3
	3	17.7	1.1	1.4
	4	19.3	10.0	0.0
	5	24.7	2.0	0.5
	6	26.2	2.5	0.8
	7	34.9	2.9	0.5
	8	44.0	7.6	0.4
	9	44.4	7.2	2.6
	10	49.2	2.4	1.1
	11	57.8	2.1	0.2
	12	65.3	11.0	0.7
	13	75.9	1.9	5.4
	14	82.0	4.8	2.6
	15	92.9	5.9	0.1
	16	96.2	3.0	14.0
	17	112.1	2.1	1.5
	18	126.2	6.8	11.2
	19	134.7	12.5	0.7
	20	136.1	1.6	15.3
	21	140.4	6.1	1.5
	22	148.6	3.1	1.0
	23	158.2	3.8	1.4
	24	162.2	0.3	20.8
	25	177.9	0.9	27.3
	26	178.6	1.8	35.6
	27	207.4	1.1	29.9
	28	220.4	2.5	104.0
	29	225.8	3.2	80.6
	30	234.5	4.3	19.7
	31	235.6	1.0	163.8
	32	238.4	4.0	7.2

33	291.3	6.6	464.9
34	296.3	2.7	34.0
35	324.7	11.1	38.7
36	330.9	5.7	18.7
37	402.6	5.8	78.6
38	407.3	4.2	144.9
39	436.8	72.2	32.9
40	441.1	18.6	37.3
41	656.5	0.2	7.3
42	662.1	0.5	7.6
43	663.3	1.5	11.4
44	664.2	1.0	9.0
45	676.1	0.1	5.2
46	680.9	0.4	7.5
47	684.8	0.5	13.6
48	685.8	0.9	10.1
49	705.4	1.1	11.7
50	716.1	9.6	12.5
51	717.6	4.8	22.3
52	718.7	7.8	27.0
53	720.1	9.4	9.5
54	722.1	16.3	31.5
55	724.1	4.7	19.8
56	726.5	4.6	15.8
57	1383.2	3.4	186.0
58	1396.4	9.0	237.5
59	1401.6	21.1	200.9
60	1403.5	23.3	257.5
61	1407.0	11.9	467.0
62	1411.0	52.2	129.0
63	1435.0	71.4	79.0
64	1448.4	41.8	126.4
65	2222.6	127.0	505.2
66	2233.0	10.9	4385.6
67	2246.3	117.6	1564.4
68	2259.1	80.2	57.0
69	2276.3	149.2	1150.1
70	2281.2	27.1	2041.8
71	2302.5	224.1	395.3
72	2313.6	19.2	1120.4

Sb3-Sb3	Mode	Freq (cm^{-1})	Raman int	IR int
	1	8.9	0.0	1.3
	2	15.7	0.0	1.5
	3	16.1	4.8	0.0
	4	23.7	0.0	1.0
	5	26.5	11.4	0.0
	6	28.5	0.0	1.9
	7	35.7	12.1	0.0
	8	42.1	0.0	2.0
	9	43.2	1.6	0.0
	10	47.2	7.4	0.0
	11	53.8	0.0	6.6
	12	57.9	14.7	0.0
	13	60.6	8.6	0.0
	14	62.1	0.0	2.4
	15	83.4	5.7	0.0
	16	83.6	0.0	5.9
	17	86.8	0.0	8.4
	18	128.4	11.6	0.0
	19	129.0	0.0	34.8
	20	133.2	9.5	0.0
	21	138.9	0.0	7.8
	22	145.2	8.9	0.0
	23	154.0	0.0	3.5
	24	158.4	6.7	0.0
	25	185.6	0.0	104.9
	26	185.9	4.3	0.6
	27	210.8	4.6	0.0
	28	213.8	0.0	2.6
	29	229.6	0.0	274.7
	30	236.7	4.4	0.0
	31	239.7	4.9	0.0
	32	240.0	0.0	112.2
	33	292.2	0.0	406.5
	34	300.3	12.8	0.0
	35	328.7	12.5	0.0
	36	330.9	0.0	114.5
	37	404.4	9.9	0.0
	38	406.2	0.0	218.2
	39	432.2	86.0	0.0
	40	433.6	0.0	57.8

41	661.9	1.0	0.4
42	662.0	0.0	17.7
43	664.4	0.9	11.0
44	664.4	1.1	8.8
45	673.2	2.3	0.0
46	674.1	0.0	20.4
47	685.0	1.0	4.5
48	685.0	0.3	14.1
49	712.0	12.7	0.1
50	712.3	0.1	21.9
51	714.7	2.9	45.9
52	714.8	10.8	12.2
53	717.4	14.2	0.0
54	717.7	0.0	14.2
55	721.0	0.0	42.4
56	721.0	11.3	0.0
57	1393.4	13.0	0.0
58	1393.8	0.0	499.2
59	1402.2	34.4	13.8
60	1402.3	1.7	282.8
61	1407.6	0.0	739.1
62	1411.0	62.3	0.1
63	1429.1	130.7	0.0
64	1435.2	0.0	227.2
65	2234.4	0.0	4532.9
66	2235.8	70.8	0.1
67	2245.3	368.6	0.0
68	2261.6	0.0	2097.2
69	2280.5	129.4	0.1
70	2283.3	0.0	3107.7
71	2305.7	257.1	0.0
72	2308.5	0.0	1208.5

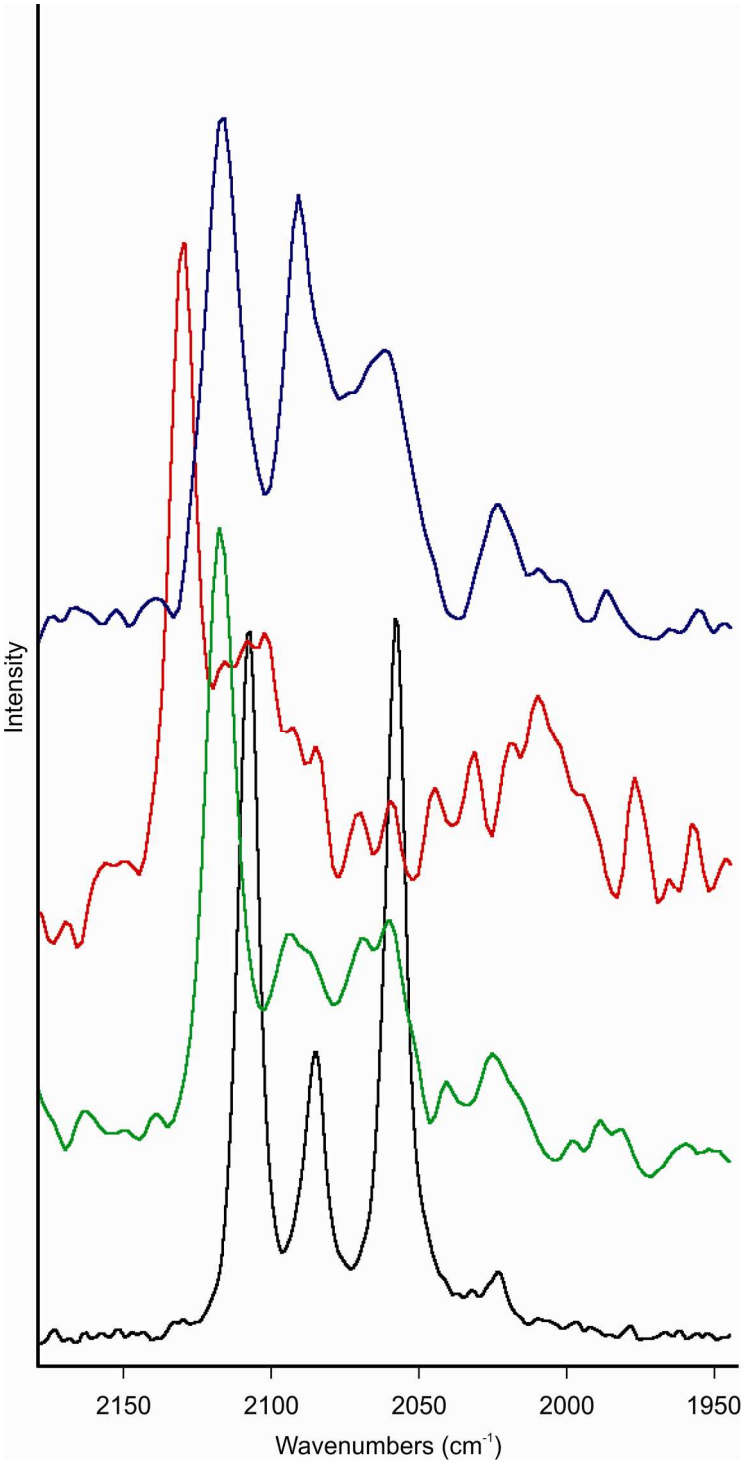

Figure S22: Antisymmetric azide stretching region in the Raman spectra of [PNP][$As(N_3)_4$]: neat (black), CH_3CN solution at -30 °C (green), SO_2 solution at -30 °C (red), frozen CH_3CN solution at -80 °C (blue).

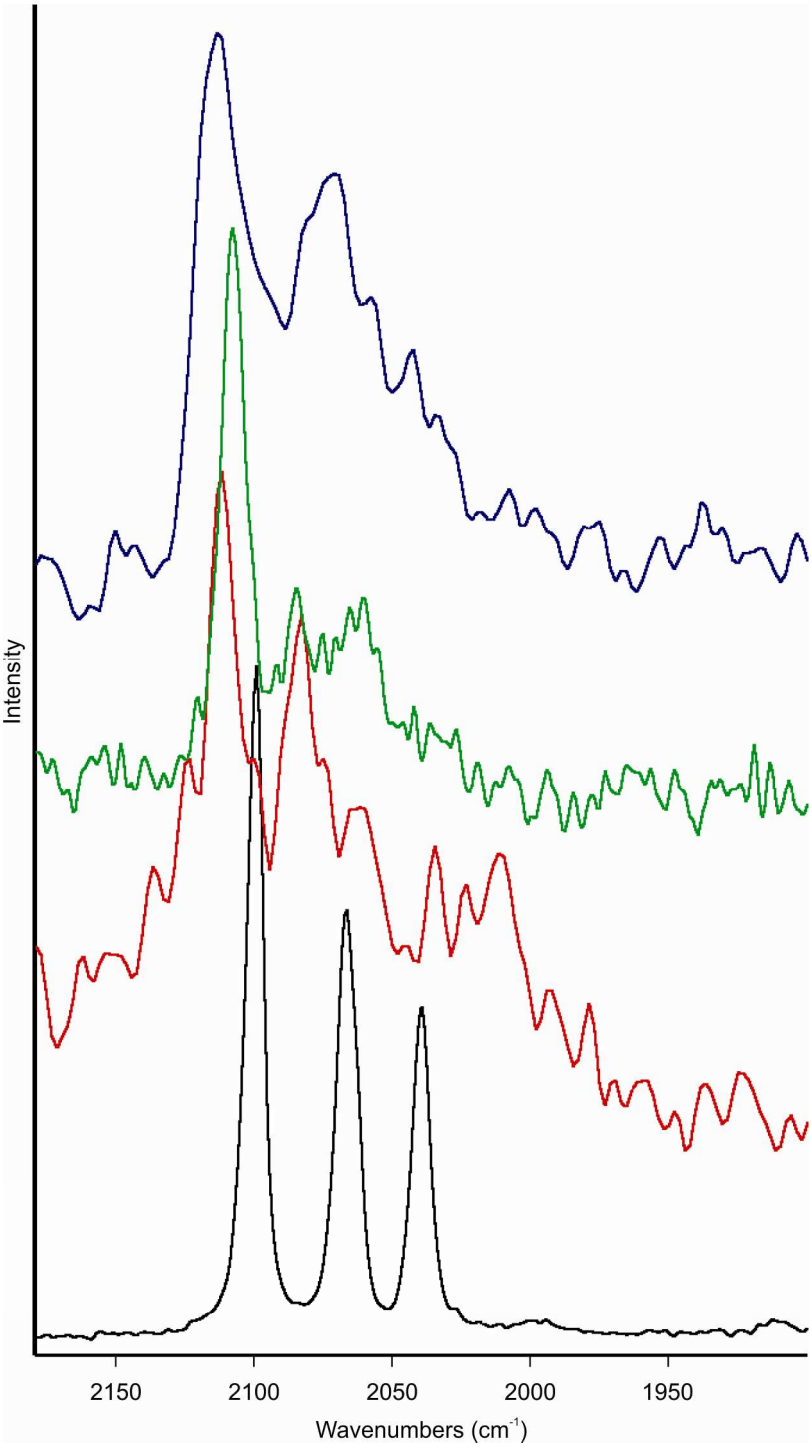

Figure S23: Antisymmetric azide stretching region in the Raman spectra of [TMA][$Sb(N_3)_4$]: neat solid (black), SO_2 solution at -30 °C (red), CH_3CN solution at -30 °C (green), frozen CH_3CN solution at -80 °C (blue).

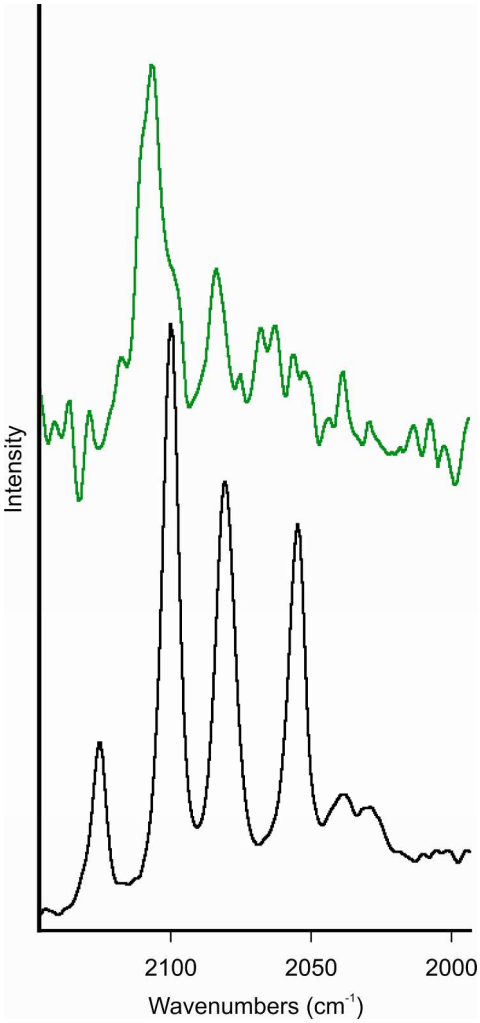

Figure S24: Antisymmetric azide stretching region in the Raman spectra of [PNP][Sb(N_3)$_4$]: neat (black) and CH_3CN solution at -30 °C (green).

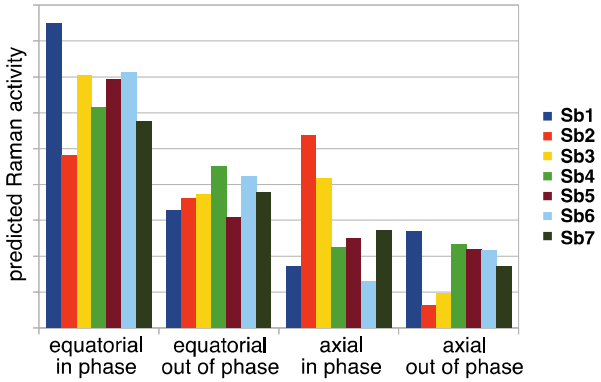

Figure S25. Theoretical Raman intensities of Sb-1-7 for the four characteristic azide

antisymmetric stretching bands, calculated at the M06-2X/cc-pwCVTZ level for the gas-phase.