Multifunctional ternary additive in bulk heterojunction OPV: in-creased device performance and stability

Trevor M. Grant,[a] Therese Gorisse,[b] Olivier Dautel,[c] Guillaume Wantz[b,†] and Benoît H. Lessard[a,†]

ELECTRONIC SUPPORTING INFO

Contents

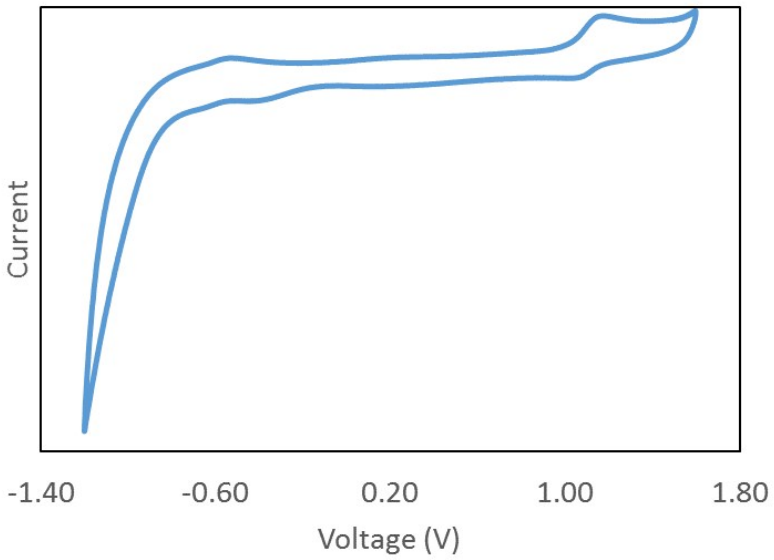

Figure S1. Characteristic cyclic voltammogram for $(HxN_3)_2$-SiPc.

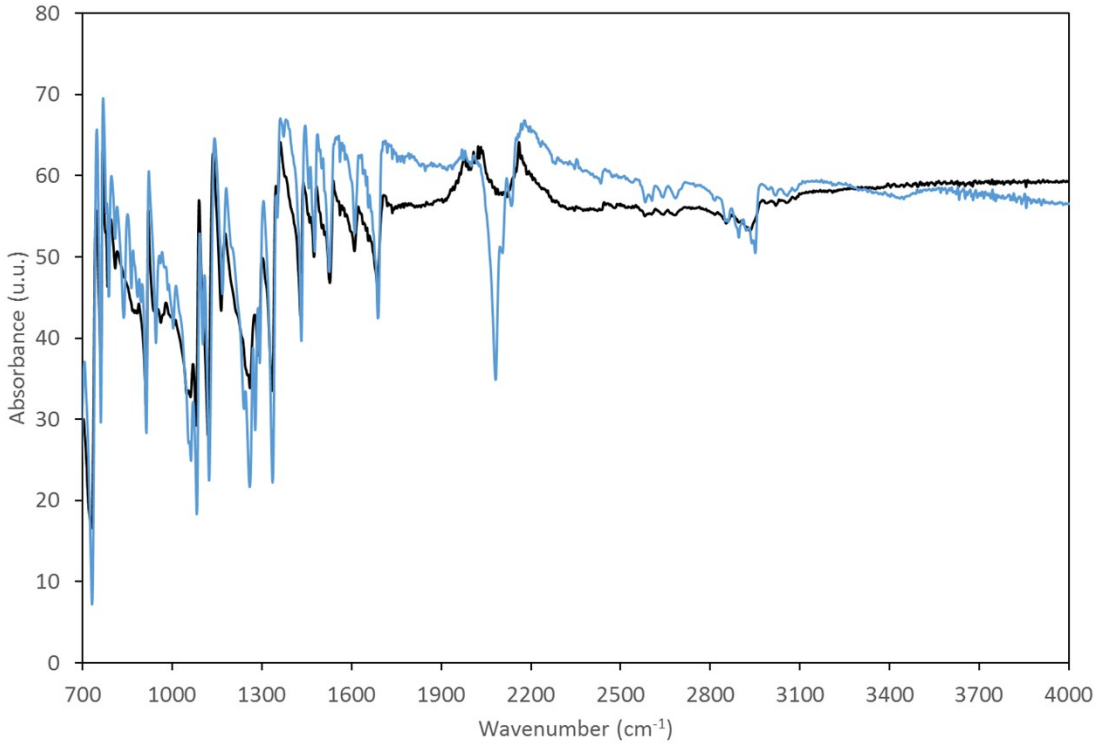

Figure S2. FTIR spectrum obtained for $(HxCl)_2$-SiPc (black) and $(HxN_3)_2$-SiPc (blue)

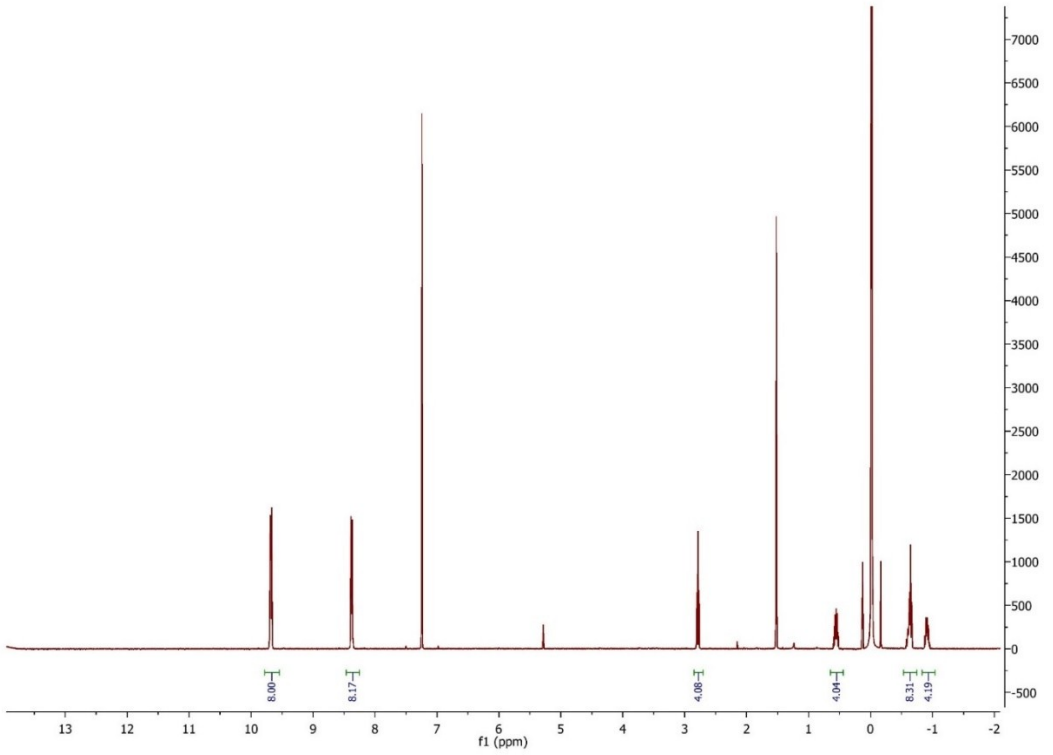

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum obtained at 296 K for $(HxCl)_2$-SiPc

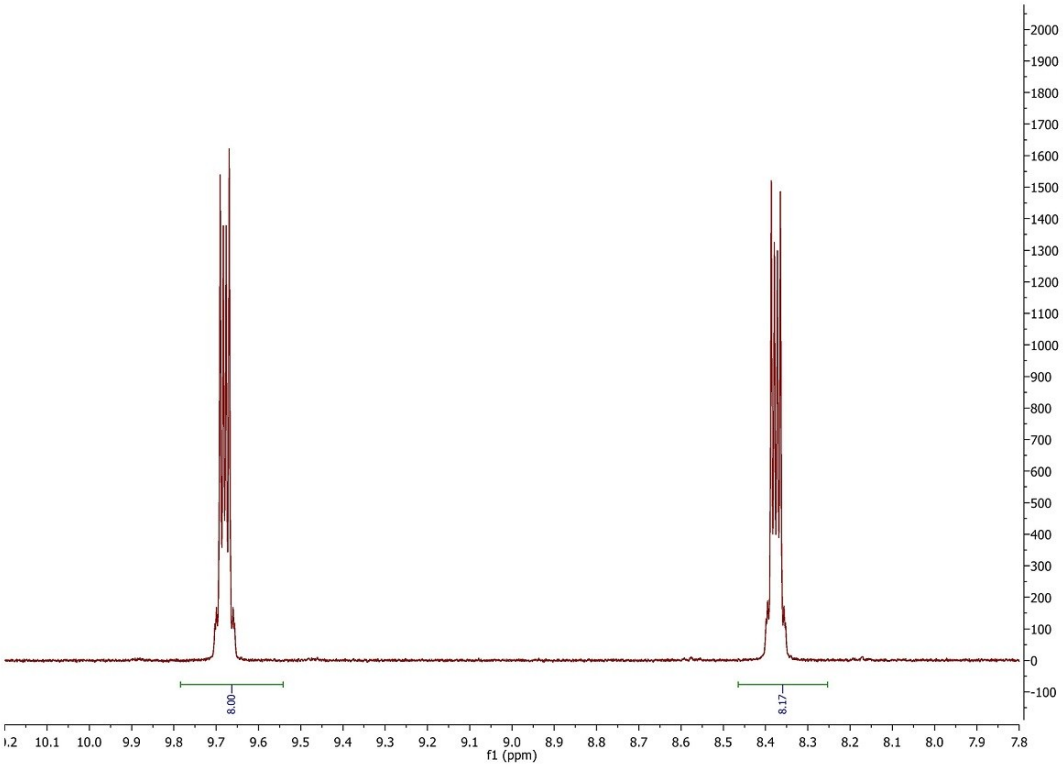

Figure S4. ^{1}H NMR (400 MHz, $CDCl_{3,}$) spectrum obtained at 296 K for $(HxCl)_2$-SiPc displaying the aromatic region.

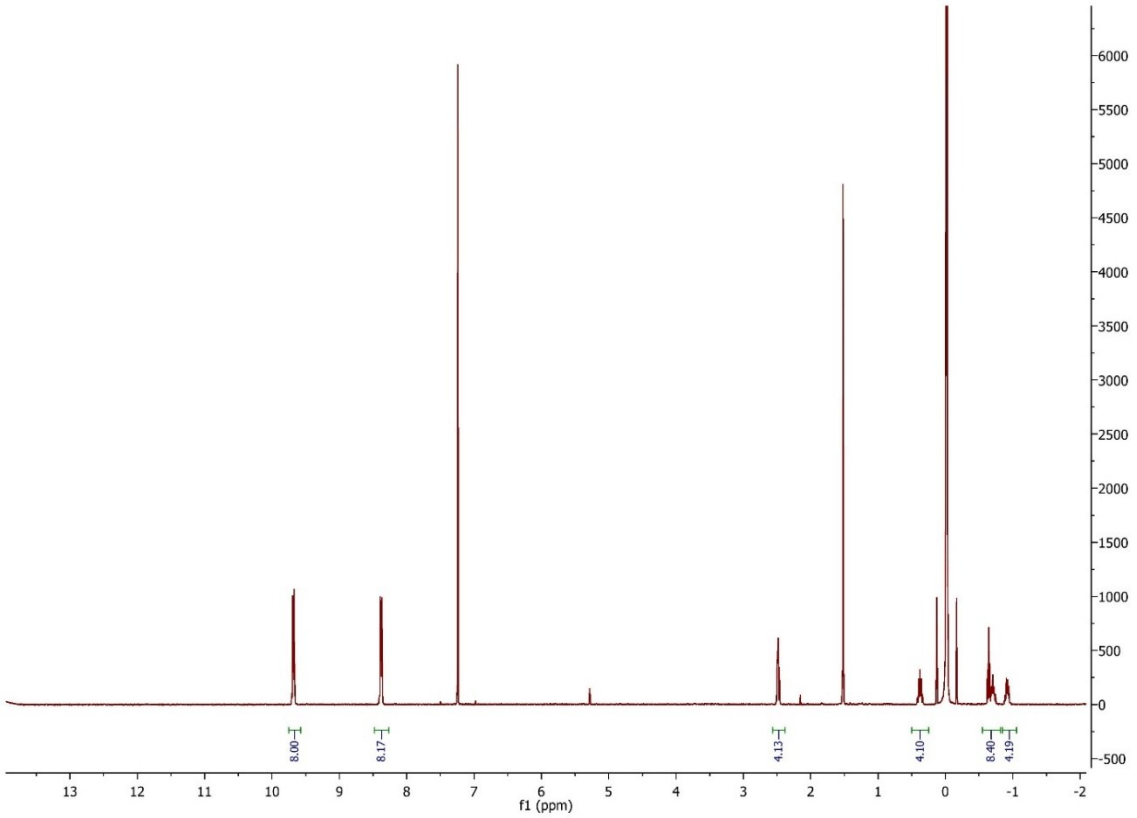

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum obtained at 296 K for $(HxN_3)_2$-SiPc

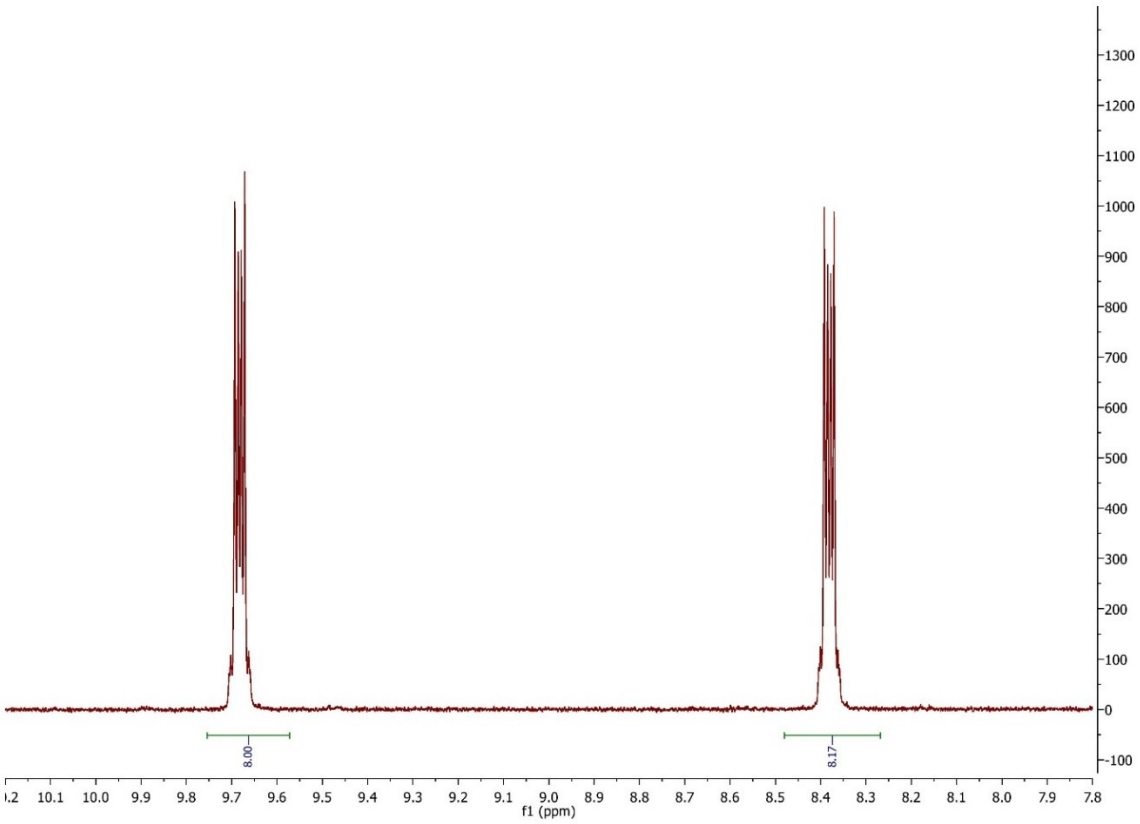

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum obtained at 296 K for $(HxN_3)_2$-SiPc displaying the aromatic region.

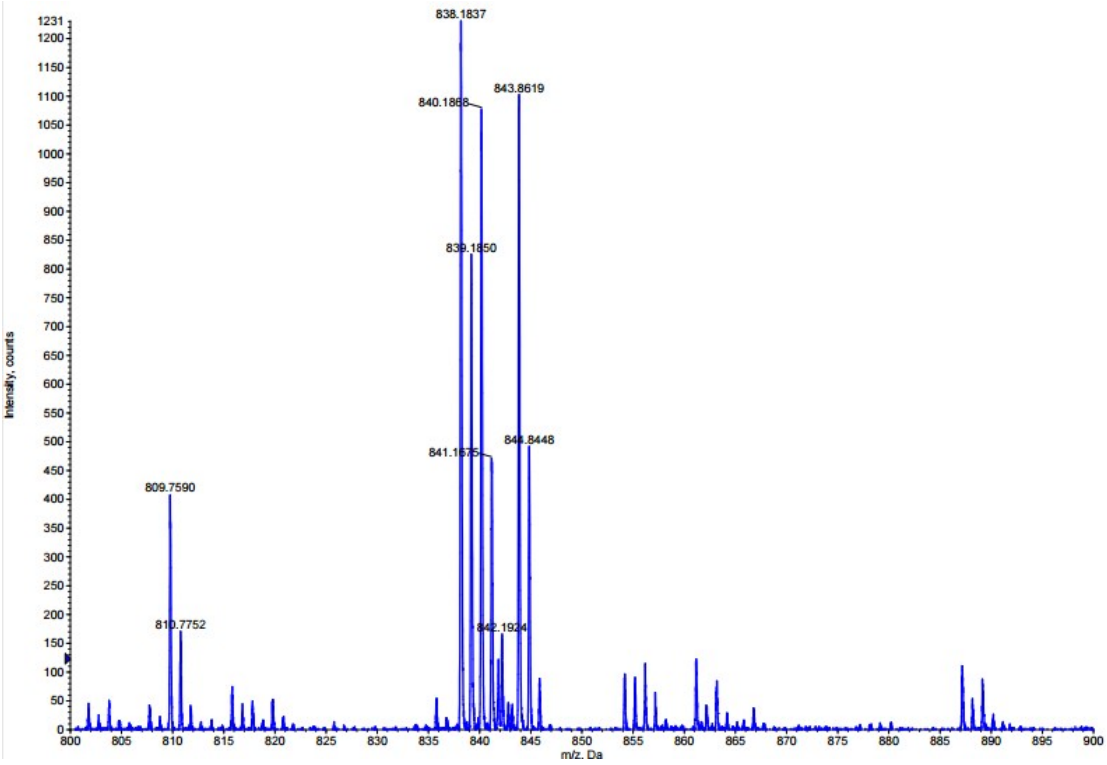

Figure S7. MS spectrum for $(HxCl)_2$-SiPc (Ion Spray)

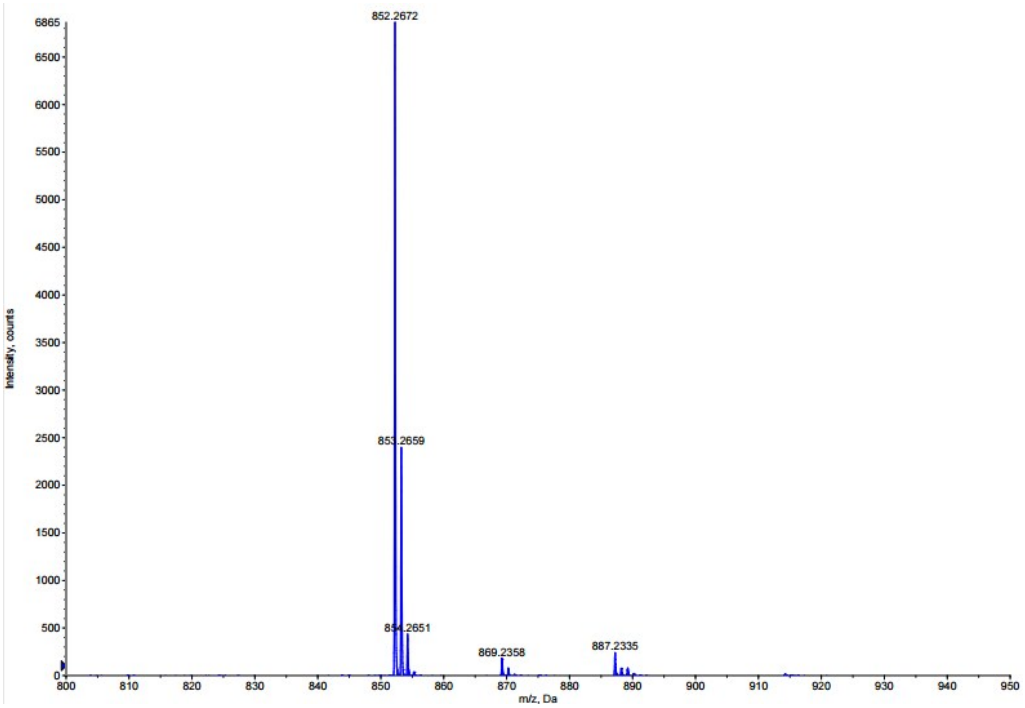

Figure S8. MS spectrum for $(HxN_3)_2$-SiPc (Ion Spray)

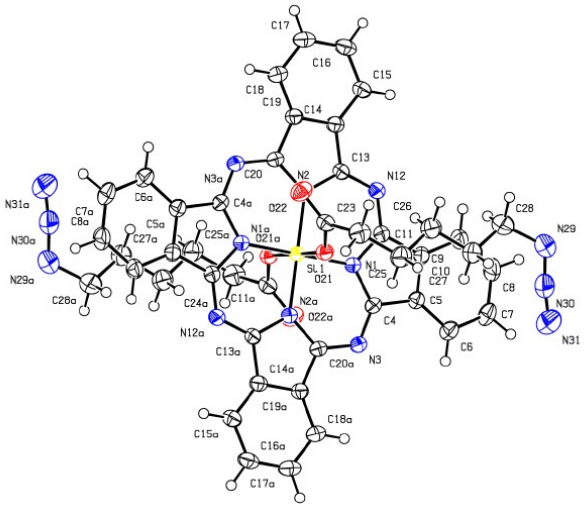

Table 1. Crystal data and structure refinement for (HxN3)2-SiPc_fin.

Identification code	shelx	
Empirical formula	C44 H36 N14 O4 Si	
Formula weight	852.96	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.4224(8) Å	α= 90°.
	b = 24.105(2) Å	β= 104.085(5)°.
	c = 8.1188(6) Å	γ = 90°.
Volume	1978.4(3) $Å^3$	
Z	2	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	0.126 mm^{-1}	
F(000)	888	
Crystal size	0.958 x 0.194 x 0.044 mm^3	
Theta range for data collection	2.015 to 28.280°.	
Index ranges	-13<=h<=13, -32<=k<=31, -10<=l<=10	
Reflections collected	33632	
Independent reflections	4900 [R(int) = 0.0511]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5801	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	4900 / 0 / 286
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1043
R indices (all data)	R1 = 0.0581, wR2 = 0.1167
Extinction coefficient	n/a
Largest diff. peak and hole	0.240 and -0.335 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (HxN3)2-SiPc_fin. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	5000	5000	5000	23(1)
N(1)	5264(1)	4466(1)	3390(1)	25(1)
N(2)	5803(1)	5552(1)	3909(1)	25(1)
N(3)	4406(1)	3634(1)	4421(2)	30(1)
C(4)	4977(1)	3906(1)	3390(2)	27(1)
C(5)	5390(2)	3632(1)	2027(2)	29(1)
C(6)	5312(2)	3080(1)	1508(2)	35(1)
C(7)	5806(2)	2949(1)	123(2)	40(1)
C(8)	6330(2)	3358(1)	-741(2)	41(1)
C(9)	6394(2)	3909(1)	-241(2)	35(1)
C(10)	5926(1)	4037(1)	1180(2)	28(1)
C(11)	5866(1)	4554(1)	2068(2)	26(1)
N(12)	6381(1)	5019(1)	1664(2)	28(1)
C(13)	6361(1)	5478(1)	2543(2)	26(1)
C(14)	6946(1)	5993(1)	2160(2)	28(1)
C(15)	7611(2)	6133(1)	920(2)	33(1)
C(16)	8046(2)	6677(1)	921(2)	38(1)
C(17)	7835(2)	7066(1)	2099(2)	37(1)
C(18)	7168(2)	6926(1)	3318(2)	33(1)
C(19)	6725(1)	6383(1)	3320(2)	28(1)
C(20)	5995(1)	6103(1)	4375(2)	27(1)
O(21)	6532(1)	4784(1)	6278(1)	28(1)
O(22)	7700(1)	5554(1)	7172(2)	41(1)
C(23)	7621(1)	5054(1)	7049(2)	30(1)

C(24)	8769(2)	4678(1)	7840(2)	41(1)
C(25)	8819(2)	4127(1)	6946(2)	43(1)
C(26)	9180(2)	4185(1)	5259(2)	45(1)
C(27)	9245(2)	3625(1)	4408(2)	47(1)
C(28)	9617(2)	3676(1)	2741(3)	51(1)
N(29)	9798(2)	3139(1)	1933(3)	67(1)
N(30)	9104(2)	2753(1)	2154(2)	54(1)
N(31)	8544(2)	2364(1)	2276(3)	80(1)

Table 3. Bond lengths [Å] and angles [°] for (HxN3)2-SiPc_fin.

Si(1)-O(21)	1.7581(10)
Si(1)-O(21)#1	1.7581(10)
Si(1)-N(1)#1	1.9007(11)
Si(1)-N(1)	1.9007(11)
Si(1)-N(2)#1	1.9025(11)
Si(1)-N(2)	1.9025(11)
N(1)-C(4)	1.3834(17)
N(1)-C(11)	1.3850(17)
N(2)-C(20)	1.3826(18)
N(2)-C(13)	1.3829(17)
N(3)-C(4)	1.3140(18)
N(3)-C(20)#1	1.3152(18)
C(4)-C(5)	1.4413(19)
C(5)-C(10)	1.387(2)
C(5)-C(6)	1.393(2)
C(6)-C(7)	1.382(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.395(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.387(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.392(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.4475(19)
C(11)-N(12)	1.3199(18)

N(12)-C(13)	1.3190(18)
C(13)-C(14)	1.4496(19)
C(14)-C(19)	1.389(2)
C(14)-C(15)	1.3951(19)
C(15)-C(16)	1.388(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.395(2)
C(16)-H(16)	0.9500
C(17)-C(18)	1.382(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.390(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.4430(19)
C(20)-N(3)#1	1.3152(18)
O(21)-C(23)	1.3270(17)
O(22)-C(23)	1.2110(18)
C(23)-C(24)	1.514(2)
C(24)-C(25)	1.521(2)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.512(3)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.524(3)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.501(3)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-N(29)	1.483(3)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
N(29)-N(30)	1.219(2)
N(30)-N(31)	1.120(2)

O(21)-Si(1)-O(21)#1	180.0
O(21)-Si(1)-N(1)#1	93.30(5)

O(21)#1-Si(1)-N(1)#1	86.70(5)
O(21)-Si(1)-N(1)	86.70(5)
O(21)#1-Si(1)-N(1)	93.30(5)
N(1)#1-Si(1)-N(1)	180.00(5)
O(21)-Si(1)-N(2)#1	87.51(5)
O(21)#1-Si(1)-N(2)#1	92.49(5)
N(1)#1-Si(1)-N(2)#1	89.98(5)
N(1)-Si(1)-N(2)#1	90.02(5)
O(21)-Si(1)-N(2)	92.49(5)
O(21)#1-Si(1)-N(2)	87.51(5)
N(1)#1-Si(1)-N(2)	90.02(5)
N(1)-Si(1)-N(2)	89.98(5)
N(2)#1-Si(1)-N(2)	180.0
C(4)-N(1)-C(11)	106.66(11)
C(4)-N(1)-Si(1)	126.41(9)
C(11)-N(1)-Si(1)	126.78(9)
C(20)-N(2)-C(13)	106.47(11)
C(20)-N(2)-Si(1)	126.55(9)
C(13)-N(2)-Si(1)	126.93(9)
C(4)-N(3)-C(20)#1	120.56(13)
N(3)-C(4)-N(1)	128.19(13)
N(3)-C(4)-C(5)	121.79(13)
N(1)-C(4)-C(5)	110.01(12)
C(10)-C(5)-C(6)	121.60(13)
C(10)-C(5)-C(4)	106.85(12)
C(6)-C(5)-C(4)	131.54(14)
C(7)-C(6)-C(5)	117.22(15)
C(7)-C(6)-H(6)	121.4
C(5)-C(6)-H(6)	121.4
C(6)-C(7)-C(8)	121.16(15)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-H(7)	119.4
C(9)-C(8)-C(7)	121.76(15)
C(9)-C(8)-H(8)	119.1
C(7)-C(8)-H(8)	119.1
C(8)-C(9)-C(10)	116.96(15)
C(8)-C(9)-H(9)	121.5

C(10)-C(9)-H(9)	121.5
C(5)-C(10)-C(9)	121.28(14)
C(5)-C(10)-C(11)	106.68(12)
C(9)-C(10)-C(11)	132.03(14)
N(12)-C(11)-N(1)	127.64(12)
N(12)-C(11)-C(10)	122.54(12)
N(1)-C(11)-C(10)	109.75(12)
C(13)-N(12)-C(11)	121.10(12)
N(12)-C(13)-N(2)	127.47(12)
N(12)-C(13)-C(14)	122.55(12)
N(2)-C(13)-C(14)	109.98(12)
C(19)-C(14)-C(15)	121.26(13)
C(19)-C(14)-C(13)	106.61(12)
C(15)-C(14)-C(13)	132.13(14)
C(16)-C(15)-C(14)	116.62(14)
C(16)-C(15)-H(15)	121.7
C(14)-C(15)-H(15)	121.7
C(15)-C(16)-C(17)	121.97(14)
C(15)-C(16)-H(16)	119.0
C(17)-C(16)-H(16)	119.0
C(18)-C(17)-C(16)	121.19(14)
C(18)-C(17)-H(17)	119.4
C(16)-C(17)-H(17)	119.4
C(17)-C(18)-C(19)	117.12(15)
C(17)-C(18)-H(18)	121.4
C(19)-C(18)-H(18)	121.4
C(14)-C(19)-C(18)	121.82(13)
C(14)-C(19)-C(20)	106.59(12)
C(18)-C(19)-C(20)	131.58(14)
N(3)#1-C(20)-N(2)	127.95(13)
N(3)#1-C(20)-C(19)	121.72(13)
N(2)-C(20)-C(19)	110.32(12)
C(23)-O(21)-Si(1)	133.03(9)
O(22)-C(23)-O(21)	124.13(14)
O(22)-C(23)-C(24)	122.08(14)
O(21)-C(23)-C(24)	113.75(13)
C(23)-C(24)-C(25)	115.85(14)

C(23)-C(24)-H(24A)	108.3
C(25)-C(24)-H(24A)	108.3
C(23)-C(24)-H(24B)	108.3
C(25)-C(24)-H(24B)	108.3
H(24A)-C(24)-H(24B)	107.4
C(26)-C(25)-C(24)	113.40(15)
C(26)-C(25)-H(25A)	108.9
C(24)-C(25)-H(25A)	108.9
C(26)-C(25)-H(25B)	108.9
C(24)-C(25)-H(25B)	108.9
H(25A)-C(25)-H(25B)	107.7
C(25)-C(26)-C(27)	112.19(15)
C(25)-C(26)-H(26A)	109.2
C(27)-C(26)-H(26A)	109.2
C(25)-C(26)-H(26B)	109.2
C(27)-C(26)-H(26B)	109.2
H(26A)-C(26)-H(26B)	107.9
C(28)-C(27)-C(26)	112.78(15)
C(28)-C(27)-H(27A)	109.0
C(26)-C(27)-H(27A)	109.0
C(28)-C(27)-H(27B)	109.0
C(26)-C(27)-H(27B)	109.0
H(27A)-C(27)-H(27B)	107.8
N(29)-C(28)-C(27)	114.61(16)
N(29)-C(28)-H(28A)	108.6
C(27)-C(28)-H(28A)	108.6
N(29)-C(28)-H(28B)	108.6
C(27)-C(28)-H(28B)	108.6
H(28A)-C(28)-H(28B)	107.6
N(30)-N(29)-C(28)	117.25(16)
N(31)-N(30)-N(29)	172.8(2)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for (HxN3)2-SiPc_fin. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	26(1)	20(1)	25(1)	-1(1)	9(1)	-2(1)
N(1)	27(1)	22(1)	27(1)	0(1)	10(1)	-2(1)
N(2)	27(1)	23(1)	27(1)	0(1)	9(1)	-2(1)
N(3)	38(1)	23(1)	33(1)	-1(1)	15(1)	-3(1)
C(4)	30(1)	22(1)	29(1)	-2(1)	8(1)	-1(1)
C(5)	31(1)	28(1)	28(1)	-1(1)	7(1)	1(1)
C(6)	41(1)	28(1)	35(1)	-3(1)	8(1)	0(1)
C(7)	51(1)	31(1)	38(1)	-10(1)	9(1)	5(1)
C(8)	49(1)	42(1)	36(1)	-8(1)	16(1)	7(1)
C(9)	39(1)	37(1)	32(1)	-2(1)	14(1)	3(1)
C(10)	27(1)	28(1)	29(1)	-2(1)	7(1)	1(1)
C(11)	28(1)	27(1)	27(1)	-1(1)	9(1)	1(1)
N(12)	31(1)	27(1)	28(1)	-1(1)	12(1)	-2(1)
C(13)	26(1)	27(1)	27(1)	2(1)	9(1)	0(1)
C(14)	28(1)	27(1)	30(1)	3(1)	8(1)	-2(1)
C(15)	34(1)	34(1)	34(1)	4(1)	14(1)	-2(1)
C(16)	36(1)	39(1)	41(1)	10(1)	14(1)	-5(1)
C(17)	36(1)	32(1)	44(1)	10(1)	8(1)	-7(1)
C(18)	37(1)	26(1)	38(1)	2(1)	10(1)	-4(1)
C(19)	29(1)	26(1)	32(1)	3(1)	9(1)	-1(1)
C(20)	31(1)	23(1)	30(1)	2(1)	9(1)	-2(1)
O(21)	27(1)	25(1)	31(1)	0(1)	7(1)	-2(1)
O(22)	40(1)	32(1)	49(1)	-6(1)	5(1)	-7(1)
C(23)	29(1)	34(1)	27(1)	-1(1)	9(1)	-4(1)
C(24)	32(1)	44(1)	44(1)	2(1)	2(1)	-1(1)
C(25)	34(1)	39(1)	56(1)	9(1)	8(1)	7(1)
C(26)	36(1)	40(1)	60(1)	2(1)	13(1)	2(1)
C(27)	42(1)	39(1)	63(1)	5(1)	20(1)	5(1)
C(28)	43(1)	47(1)	67(1)	1(1)	21(1)	-4(1)
N(29)	67(1)	55(1)	95(2)	-10(1)	50(1)	-5(1)
N(30)	49(1)	48(1)	70(1)	-7(1)	25(1)	6(1)
N(31)	80(1)	47(1)	125(2)	-11(1)	45(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (HxN3)2-SiPc_fin.

	x	y	z	U(eq)
H(6)	4934	2804	2082	42
H(7)	5789	2575	-247	48
H(8)	6651	3255	-1698	50
H(9)	6743	4187	-840	42
H(15)	7758	5869	117	40
H(16)	8501	6788	94	45
H(17)	8155	7434	2064	45
H(18)	7019	7190	4120	40
H(24A)	8735	4601	9027	50
H(24B)	9602	4880	7880	50
H(25A)	9475	3883	7694	52
H(25B)	7944	3945	6757	52
H(26A)	10049	4371	5440	54
H(26B)	8515	4422	4498	54
H(27A)	9901	3387	5178	56
H(27B)	8372	3441	4219	56
H(28A)	8920	3890	1948	61
H(28B)	10450	3890	2921	61

Table 6. Torsion angles [°] for (HxN3)2-SiPc_fin.

C(20)#1-N(3)-C(4)-N(1)	1.3(2)
C(20)#1-N(3)-C(4)-C(5)	-178.08(14)
C(11)-N(1)-C(4)-N(3)	179.87(14)
Si(1)-N(1)-C(4)-N(3)	4.1(2)
C(11)-N(1)-C(4)-C(5)	-0.70(16)
Si(1)-N(1)-C(4)-C(5)	-176.47(10)
N(3)-C(4)-C(5)-C(10)	178.91(14)
N(1)-C(4)-C(5)-C(10)	-0.57(16)

N(3)-C(4)-C(5)-C(6)	-0.2(3)
N(1)-C(4)-C(5)-C(6)	-179.71(16)
C(10)-C(5)-C(6)-C(7)	0.8(2)
C(4)-C(5)-C(6)-C(7)	179.86(16)
C(5)-C(6)-C(7)-C(8)	-1.6(2)
C(6)-C(7)-C(8)-C(9)	0.8(3)
C(7)-C(8)-C(9)-C(10)	0.7(3)
C(6)-C(5)-C(10)-C(9)	0.7(2)
C(4)-C(5)-C(10)-C(9)	-178.51(14)
C(6)-C(5)-C(10)-C(11)	-179.22(14)
C(4)-C(5)-C(10)-C(11)	1.54(16)
C(8)-C(9)-C(10)-C(5)	-1.5(2)
C(8)-C(9)-C(10)-C(11)	178.45(16)
C(4)-N(1)-C(11)-N(12)	-175.32(14)
Si(1)-N(1)-C(11)-N(12)	0.4(2)
C(4)-N(1)-C(11)-C(10)	1.67(16)
Si(1)-N(1)-C(11)-C(10)	177.42(9)
C(5)-C(10)-C(11)-N(12)	175.14(13)
C(9)-C(10)-C(11)-N(12)	-4.8(3)
C(5)-C(10)-C(11)-N(1)	-2.04(16)
C(9)-C(10)-C(11)-N(1)	178.02(15)
N(1)-C(11)-N(12)-C(13)	-0.4(2)
C(10)-C(11)-N(12)-C(13)	-177.06(13)
C(11)-N(12)-C(13)-N(2)	-2.0(2)
C(11)-N(12)-C(13)-C(14)	178.46(13)
C(20)-N(2)-C(13)-N(12)	-178.29(14)
Si(1)-N(2)-C(13)-N(12)	4.3(2)
C(20)-N(2)-C(13)-C(14)	1.27(15)
Si(1)-N(2)-C(13)-C(14)	-176.17(9)
N(12)-C(13)-C(14)-C(19)	179.31(13)
N(2)-C(13)-C(14)-C(19)	-0.28(16)
N(12)-C(13)-C(14)-C(15)	-0.1(3)
N(2)-C(13)-C(14)-C(15)	-179.66(15)
C(19)-C(14)-C(15)-C(16)	0.6(2)
C(13)-C(14)-C(15)-C(16)	179.88(15)
C(14)-C(15)-C(16)-C(17)	0.1(2)
C(15)-C(16)-C(17)-C(18)	-0.6(3)

C(16)-C(17)-C(18)-C(19)	0.3(2)
C(15)-C(14)-C(19)-C(18)	-0.9(2)
C(13)-C(14)-C(19)-C(18)	179.66(14)
C(15)-C(14)-C(19)-C(20)	178.67(14)
C(13)-C(14)-C(19)-C(20)	-0.79(16)
C(17)-C(18)-C(19)-C(14)	0.4(2)
C(17)-C(18)-C(19)-C(20)	-179.00(15)
C(13)-N(2)-C(20)-N(3)#1	177.74(14)
Si(1)-N(2)-C(20)-N(3)#1	-4.8(2)
C(13)-N(2)-C(20)-C(19)	-1.78(16)
Si(1)-N(2)-C(20)-C(19)	175.67(9)
C(14)-C(19)-C(20)-N(3)#1	-177.93(14)
C(18)-C(19)-C(20)-N(3)#1	1.6(3)
C(14)-C(19)-C(20)-N(2)	1.63(17)
C(18)-C(19)-C(20)-N(2)	-178.89(15)
N(1)#1-Si(1)-O(21)-C(23)	-52.35(12)
N(1)-Si(1)-O(21)-C(23)	127.65(12)
N(2)#1-Si(1)-O(21)-C(23)	-142.19(12)
N(2)-Si(1)-O(21)-C(23)	37.81(12)
Si(1)-O(21)-C(23)-O(22)	9.7(2)
Si(1)-O(21)-C(23)-C(24)	-172.61(10)
O(22)-C(23)-C(24)-C(25)	-151.12(16)
O(21)-C(23)-C(24)-C(25)	31.13(19)
C(23)-C(24)-C(25)-C(26)	71.08(19)
C(24)-C(25)-C(26)-C(27)	179.05(15)
C(25)-C(26)-C(27)-C(28)	-179.35(16)
C(26)-C(27)-C(28)-N(29)	175.29(17)
C(27)-C(28)-N(29)-N(30)	33.0(3)

Symmetry transformations used to generate equivalent atoms:

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

Table 7. Hydrogen bonds for (HxN3)2-SiPc_fin [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(28)-H(28B)...O(22)#2	0.99	2.36	3.343(2)	169.7
C(28)-H(28B)...O(22)#2	0.99	2.36	3.343(2)	169.7

Symmetry transformations used to generate equivalent atoms:

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