Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

yo

Supporting Information for

A Luminescent and Dichroic Hexagermane

Kimberly D. Roewe, Arnold L. Rheingold, and Charles S. Weinert*

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Experimental Details

Preparation of 3: A suspension of Ge_4Ph_8 (0.30 g, 0.33 mmol)[14] in benzene (50 mL) was titrated with a 0.059 M solution of bromine in benzene until the solution remained colorless. The volatiles were removed *in vacuo* and the resulting solid was washed with Et_2O (3 x 5 mL) and dried *in vacuo* to yield **3** (0.31 g, 89 %) as a white solid. ^{1}H NMR (C_6D_6, 25 ºC) δ 7.60 (d, *J* = 7.8 Hz, 8 H, *o*-C_6H_5), 7.41 (d, *J* = 7.5 Hz, 8 H, *o*-C_6H_5), 7.06 – 6.90 (m, 24 H, *m*-C_6H_5 and *p*-C_6H_5) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 136.7 (*ipso*-C_6H_5), 134.7 (*ipso*-C_6H_5), 130.0 (*o*-C_6H_5), 129.4 (*o*-C_6H_5), 128.8 (*m*-C_6H_5), 128.6 (*m*-C_6H_5), 128.1 (*p*-C_6H_5), 127.9 (*p*-C_6H_5) ppm. UV/Vis (CH_2Cl_2): λ_{max} 281 nm (ε 8.4 x 10^4 M^{-1} cm^{-1}). Anal. Calcd. for $C_{48}H_{40}Br_2Ge_4$: C, 54.00; H, 3.78. Found: C, 53.87; H, 3.83.

Preparation of 4: To a solution of **3** (1.05 g, 0.984 mmol) in Et_2O (60 mL) was added $LiAlH_4$ (0.08 g, 2 mmol) under blowing nitrogen. The reaction mixture was stirred for 18 h at room temperature and the volatiles were removed *in vacuo*. The resulting material was taken up in benzene and filtered through Celite. The benzene was removed *in vacuo* and the resulting solid was washed with hexane (3 x 5 mL) and dried *in vacuo* to yield **4** (0.75 g, 84 %) as a white solid. ^{1}H NMR (C_6D_6, 25 ºC) δ 7.50 (d, *J* = 6.3 Hz, 8 H, *o*-C_6H_5), 7.38 (d, *J* = 6.3 Hz, 8 H, *o*-C_6H_5), 7.04 – 6.95 (m, 24 H, *m*-C_6H_5 and *p*-C_6H_5), 5.63 (s, 2H, -Ge-*H*) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 136.5 (*ipso*-C_6H_5), 136.0 (*ipso*-C_6H_5), 128.9 (*o*-C_6H_5), 128.8 (*o*-C_6H_5), 128.5 (*m*-C_6H_5), 128.3 (*m*-C_6H_5), 128.1 (*p*-C_6H_5), 127.7 (*p*-C_6H_5) ppm. Anal. Calcd. for $C_{48}H_{42}Ge_4$: C, 63.37; H, 4.66. Found: C, 63.26; H, 4.59.

Preparation of 1: To a solution of $Pr^i_3GeNMe_2$ (0.22 g, 0.90 mmol)[29] in CH_3CN (15 mL) was added a solution of **4** (0.40 g, 0.45 mmol) in CH_3CN (15 mL). The reaction mixture was sealed

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

in a Schlenk tube and was stirred in an oil bath at 90 ºC for 72 h, after which time a white precipitate was present. The reaction mixture was cooled and the solid was collected by filtration and washed with hexane (3 x 5 mL) to yield **1** (0.23 g, 40. %) as a white solid. ^{1}H NMR (C_6D_6, 25 ºC) δ 7.39 (d, *J* = 7.5 Hz, 8 H, *o*-C_6H_5), 7.34 (d, *J* = 7.5 Hz, 8 H, *o*-C_6H_5), 7.15 – 6.96 (m, 24 H, *m*-C_6H_5 and *p*-C_6H_5), 1.48 (sept, *J* = 7.2 Hz, 6H, -C*H*$(CH_3)_2$), 0.89 (d, *J* = 7.2 Hz, 18 H, -CH(C*H*$_3)_2$) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 137.3 (*ipso*-C_6H_5), 137.0 (*ipso*-C_6H_5), 128.3 (*o*-C_6H_5), 128.2 (*o*-C_6H_5), 128.1 (*m*-C_6H_5), 127.9 (*m*-C_6H_5), 127.7 (*p*-C_6H_5), 127.6 (*p*-C_6H_5), 21.2 (-*C*H$(CH_3)_2$), 18.2 (-CH(*C*$H_3)_2$) ppm. Anal. Calcd. for $C_{66}H_{82}Ge_6$: C, 60.44; H, 6.31. Found: C, 60.36; H, 6.36.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Crystallographic Data for $Pr^{i}_{3}Ge(GePh_2)_4GePr^{i}_{3}$ (1)

Table 1. Crystal data and structure refinement for wein145.

Identification code	wein145	
Empirical formula	C66 H82 Ge6	
Formula weight	1310.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0685(7) Å	α= 97.447(2)°
	b = 11.3771(6) Å	β= 91.495(2)°
	c = 12.7949(8) Å	γ = 108.292(2)°
Volume	1513.09(16) $Å^3$	
Z	1	
Density (calculated)	1.439 g/cm^3	
Absorption coefficient	2.980 mm^{-1}	
F(000)	670	
Crystal size	0.30 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.91 to 28.36°	
Index ranges	-14<=h<=12, -11<=k<=15, -17<=l<=16	
Reflections collected	16375	
Independent reflections	7179 [R(int) = 0.0221]	
Completeness to theta = 25.00°	97.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.5871 and 0.4684	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7179 / 0 / 325	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0197, wR2 = 0.0472	
R indices (all data)	R1 = 0.0244, wR2 = 0.0487	
Largest diff. peak and hole	0.397 and -0.366 e $Å^{-3}$	

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for wein145. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ge(1)	7049(1)	8530(1)	8177(1)	12(1)
Ge(2)	5714(1)	6420(1)	7357(1)	9(1)
Ge(3)	5198(1)	6089(1)	5429(1)	9(1)
C(1)	8837(1)	8597(1)	8534(1)	16(1)
C(2)	8990(2)	7878(2)	9437(1)	24(1)
C(3)	9478(2)	8189(2)	7569(1)	19(1)
C(4)	6303(2)	9023(2)	9494(1)	20(1)
C(5)	7199(2)	10243(2)	10122(2)	30(1)
C(6)	5912(2)	7995(2)	10196(1)	26(1)
C(7)	7087(2)	9751(1)	7181(1)	20(1)
C(8)	5971(2)	10274(2)	7307(2)	24(1)
C(9)	8359(2)	10813(2)	7275(2)	30(1)
C(10)	3993(1)	5998(1)	7879(1)	13(1)
C(11)	3298(2)	4757(1)	7972(1)	18(1)
C(12)	2033(2)	4440(2)	8235(1)	24(1)
C(13)	1445(2)	5348(2)	8414(1)	24(1)
C(14)	2121(2)	6582(2)	8333(1)	19(1)
C(15)	3382(2)	6900(1)	8066(1)	14(1)
C(16)	6509(1)	5223(1)	7773(1)	12(1)
C(17)	7376(1)	4858(1)	7140(1)	14(1)
C(18)	8037(2)	4097(2)	7472(1)	20(1)
C(19)	7842(2)	3704(2)	8455(1)	22(1)
C(20)	6975(2)	4044(2)	9089(1)	21(1)
C(21)	6312(2)	4791(1)	8747(1)	17(1)
C(22)	6421(1)	7219(1)	4624(1)	12(1)
C(23)	7734(2)	7600(1)	4885(1)	17(1)
C(24)	8587(2)	8397(2)	4303(2)	24(1)
C(25)	8140(2)	8829(2)	3462(2)	23(1)
C(26)	6841(2)	8458(1)	3188(1)	19(1)
C(27)	5988(2)	7646(1)	3758(1)	14(1)
C(28)	3652(1)	6591(1)	5401(1)	13(1)

C(29)	2462(2)	5775(2)	5591(1)	18(1)
C(30)	1402(2)	6186(2)	5673(1)	26(1)
C(31)	1515(2)	7411(2)	5568(2)	32(1)
C(32)	2677(2)	8233(2)	5395(2)	28(1)
C(33)	3745(2)	7832(2)	5319(1)	19(1)

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Table 3. Bond lengths [Å] and angles [°] for wein145.

Ge(1)-C(4)	1.9892(16)	C(13)-C(14)	1.387(2)
Ge(1)-C(7)	1.9948(16)	C(14)-C(15)	1.391(2)
Ge(1)-C(1)	1.9952(16)	C(16)-C(21)	1.396(2)
Ge(1)-Ge(2)	2.4670(2)	C(16)-C(17)	1.397(2)
Ge(2)-C(16)	1.9552(15)	C(17)-C(18)	1.393(2)
Ge(2)-C(10)	1.9697(15)	C(18)-C(19)	1.389(2)
Ge(2)-Ge(3)	2.4715(3)	C(19)-C(20)	1.385(3)
Ge(3)-C(22)	1.9666(15)	C(20)-C(21)	1.387(2)
Ge(3)-C(28)	1.9682(15)	C(22)-C(27)	1.397(2)
Ge(3)-Ge(3)#1	2.4745(3)	C(22)-C(23)	1.398(2)
C(1)-C(3)	1.532(2)	C(23)-C(24)	1.394(2)
C(1)-C(2)	1.534(2)	C(24)-C(25)	1.381(3)
C(4)-C(6)	1.528(3)	C(25)-C(26)	1.386(2)
C(4)-C(5)	1.536(2)	C(26)-C(27)	1.393(2)
C(7)-C(9)	1.531(2)	C(28)-C(33)	1.400(2)
C(7)-C(8)	1.534(2)	C(28)-C(29)	1.401(2)
C(10)-C(15)	1.396(2)	C(29)-C(30)	1.394(2)
C(10)-C(11)	1.402(2)	C(30)-C(31)	1.385(3)
C(11)-C(12)	1.394(2)	C(31)-C(32)	1.375(3)
C(12)-C(13)	1.383(3)	C(32)-C(33)	1.397(2)

C(4)-Ge(1)-C(7)	108.99(7)	C(22)-Ge(3)-Ge(2)	115.68(4)
C(4)-Ge(1)-C(1)	108.74(7)	C(28)-Ge(3)-Ge(2)	99.69(4)
C(7)-Ge(1)-C(1)	108.48(7)	C(22)-Ge(3)-Ge(3)#1	108.47(4)
C(4)-Ge(1)-Ge(2)	109.19(5)	C(28)-Ge(3)-Ge(3)#1	112.43(4)
C(7)-Ge(1)-Ge(2)	109.49(5)	Ge(2)-Ge(3)-Ge(3)#1	114.153(10)
C(1)-Ge(1)-Ge(2)	111.91(4)	C(3)-C(1)-C(2)	109.86(14)
C(16)-Ge(2)-C(10)	107.95(6)	C(3)-C(1)-Ge(1)	112.47(11)
C(16)-Ge(2)-Ge(1)	107.71(4)	C(2)-C(1)-Ge(1)	114.69(11)
C(10)-Ge(2)-Ge(1)	110.80(4)	C(6)-C(4)-C(5)	110.79(15)
C(16)-Ge(2)-Ge(3)	111.71(4)	C(6)-C(4)-Ge(1)	113.61(12)
C(10)-Ge(2)-Ge(3)	100.93(4)	C(5)-C(4)-Ge(1)	111.31(11)
Ge(1)-Ge(2)-Ge(3)	117.330(8)	C(9)-C(7)-C(8)	110.75(13)
C(22)-Ge(3)-C(28)	105.92(6)	C(9)-C(7)-Ge(1)	112.73(12)

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

C(8)-C(7)-Ge(1)	111.64(11)	C(27)-C(22)-C(23)	118.27(14)
C(15)-C(10)-C(11)	117.93(14)	C(27)-C(22)-Ge(3)	120.13(11)
C(15)-C(10)-Ge(2)	121.04(11)	C(23)-C(22)-Ge(3)	121.60(12)
C(11)-C(10)-Ge(2)	120.73(12)	C(24)-C(23)-C(22)	120.80(15)
C(12)-C(11)-C(10)	120.70(16)	C(25)-C(24)-C(23)	120.09(16)
C(13)-C(12)-C(11)	120.38(16)	C(24)-C(25)-C(26)	119.99(15)
C(12)-C(13)-C(14)	119.71(15)	C(25)-C(26)-C(27)	120.02(15)
C(13)-C(14)-C(15)	120.01(16)	C(26)-C(27)-C(22)	120.80(15)
C(14)-C(15)-C(10)	121.26(15)	C(33)-C(28)-C(29)	117.99(14)
C(21)-C(16)-C(17)	117.99(14)	C(33)-C(28)-Ge(3)	120.09(12)
C(21)-C(16)-Ge(2)	121.11(12)	C(29)-C(28)-Ge(3)	121.47(11)
C(17)-C(16)-Ge(2)	120.69(11)	C(30)-C(29)-C(28)	120.68(16)
C(18)-C(17)-C(16)	121.26(15)	C(31)-C(30)-C(29)	120.17(17)
C(19)-C(18)-C(17)	119.49(16)	C(32)-C(31)-C(30)	120.16(16)
C(20)-C(19)-C(18)	120.08(15)	C(31)-C(32)-C(33)	120.05(17)
C(19)-C(20)-C(21)	120.04(16)	C(32)-C(33)-C(28)	120.93(17)
C(20)-C(21)-C(16)	121.12(15)		

Symmetry transformations used to generate equivalent atoms:

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

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for wein145. 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}
Ge(1)	10(1)	11(1)	14(1)	-1(1)	2(1)	3(1)
Ge(2)	10(1)	10(1)	9(1)	1(1)	1(1)	3(1)
Ge(3)	9(1)	10(1)	9(1)	1(1)	1(1)	4(1)
C(1)	11(1)	16(1)	20(1)	0(1)	0(1)	2(1)
C(2)	16(1)	30(1)	23(1)	5(1)	-3(1)	4(1)
C(3)	15(1)	17(1)	25(1)	3(1)	3(1)	7(1)
C(4)	14(1)	23(1)	19(1)	-7(1)	1(1)	3(1)
C(5)	25(1)	27(1)	29(1)	-13(1)	3(1)	4(1)
C(6)	20(1)	35(1)	15(1)	-3(1)	4(1)	1(1)
C(7)	23(1)	14(1)	24(1)	4(1)	6(1)	8(1)
C(8)	22(1)	20(1)	33(1)	7(1)	1(1)	10(1)
C(9)	24(1)	18(1)	52(1)	13(1)	14(1)	9(1)
C(10)	12(1)	16(1)	8(1)	0(1)	0(1)	3(1)
C(11)	19(1)	15(1)	17(1)	0(1)	4(1)	3(1)
C(12)	18(1)	22(1)	24(1)	1(1)	5(1)	-4(1)
C(13)	11(1)	36(1)	19(1)	0(1)	3(1)	3(1)
C(14)	15(1)	29(1)	14(1)	-1(1)	-1(1)	12(1)
C(15)	14(1)	17(1)	11(1)	0(1)	-1(1)	5(1)
C(16)	11(1)	9(1)	13(1)	0(1)	-2(1)	1(1)
C(17)	14(1)	14(1)	14(1)	0(1)	-1(1)	3(1)
C(18)	17(1)	16(1)	28(1)	-1(1)	1(1)	7(1)
C(19)	20(1)	16(1)	32(1)	7(1)	-5(1)	7(1)
C(20)	21(1)	20(1)	20(1)	10(1)	-2(1)	2(1)
C(21)	16(1)	18(1)	15(1)	4(1)	1(1)	5(1)
C(22)	15(1)	9(1)	12(1)	0(1)	3(1)	4(1)
C(23)	15(1)	18(1)	19(1)	4(1)	2(1)	5(1)
C(24)	14(1)	24(1)	31(1)	8(1)	4(1)	2(1)
C(25)	22(1)	19(1)	29(1)	11(1)	12(1)	5(1)
C(26)	27(1)	17(1)	15(1)	5(1)	4(1)	9(1)
C(27)	17(1)	14(1)	13(1)	0(1)	1(1)	7(1)
C(28)	14(1)	19(1)	8(1)	-2(1)	-1(1)	9(1)

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

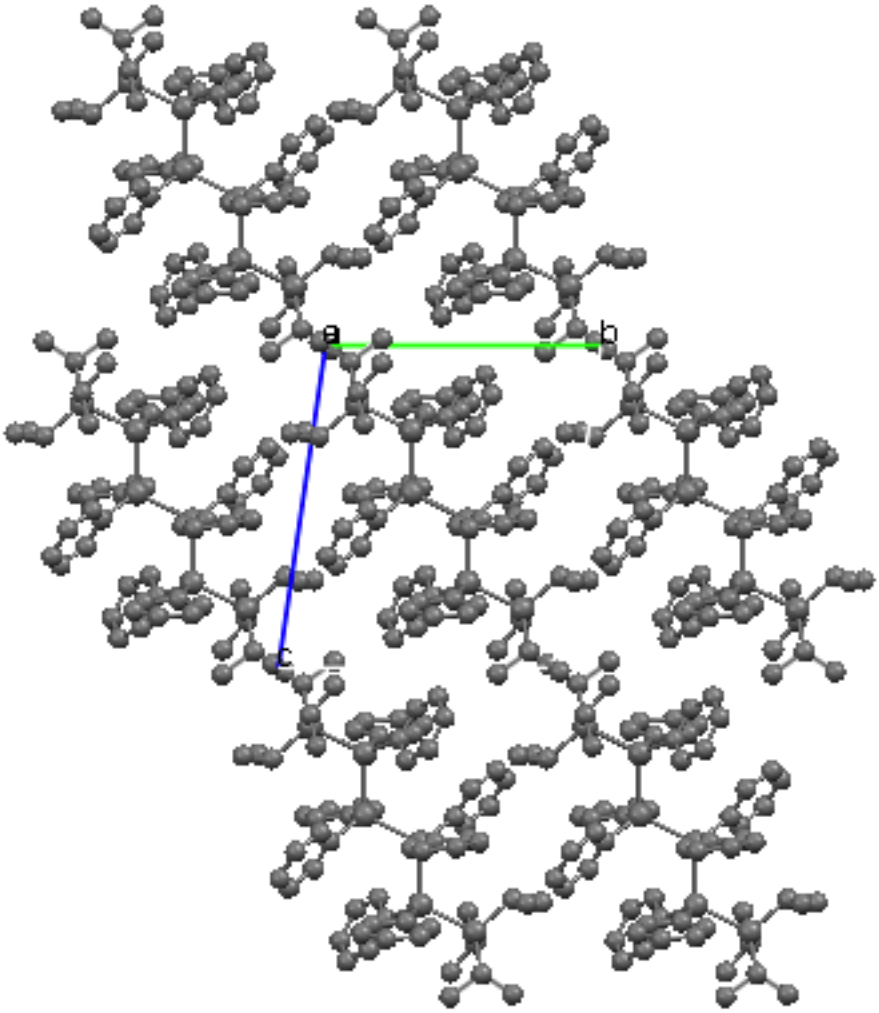
C(29)	14(1)	26(1)	12(1)	-3(1)	-1(1)	7(1)
C(30)	14(1)	49(1)	14(1)	-5(1)	-1(1)	11(1)
C(31)	27(1)	60(1)	19(1)	-1(1)	0(1)	32(1)
C(32)	40(1)	37(1)	21(1)	3(1)	3(1)	30(1)
C(33)	23(1)	23(1)	16(1)	1(1)	1(1)	14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for wein145.

	x	y	z	U(eq)
H(1A)	9329	9497	8780	19
H(2A)	9891	7959	9562	36
H(2B)	8489	6993	9246	36
H(2C)	8685	8224	10081	36
H(3A)	10351	8237	7783	28
H(3B)	9499	8741	7038	28
H(3C)	8993	7326	7268	28
H(4A)	5509	9195	9275	24
H(5A)	6808	10461	10765	45
H(5B)	7348	10916	9687	45
H(5C)	8014	10128	10313	45
H(6A)	5554	8297	10829	38
H(6B)	6662	7773	10405	38
H(6C)	5270	7256	9804	38
H(7A)	6981	9284	6449	24
H(8A)	6018	10868	6808	36
H(8B)	6017	10701	8030	36
H(8C)	5163	9586	7164	36
H(9A)	8328	11385	6771	45
H(9B)	9050	10464	7119	45
H(9C)	8514	11271	7995	45
H(11A)	3693	4126	7854	21
H(12A)	1572	3594	8292	29
H(13A)	582	5128	8591	28
H(14A)	1723	7210	8460	23
H(15A)	3836	7747	8011	17
H(17A)	7517	5134	6470	17
H(18A)	8616	3850	7029	24
H(19A)	8303	3201	8694	26
H(20A)	6835	3766	9757	25
H(21A)	5713	5013	9184	20
H(23A)	8049	7312	5466	21

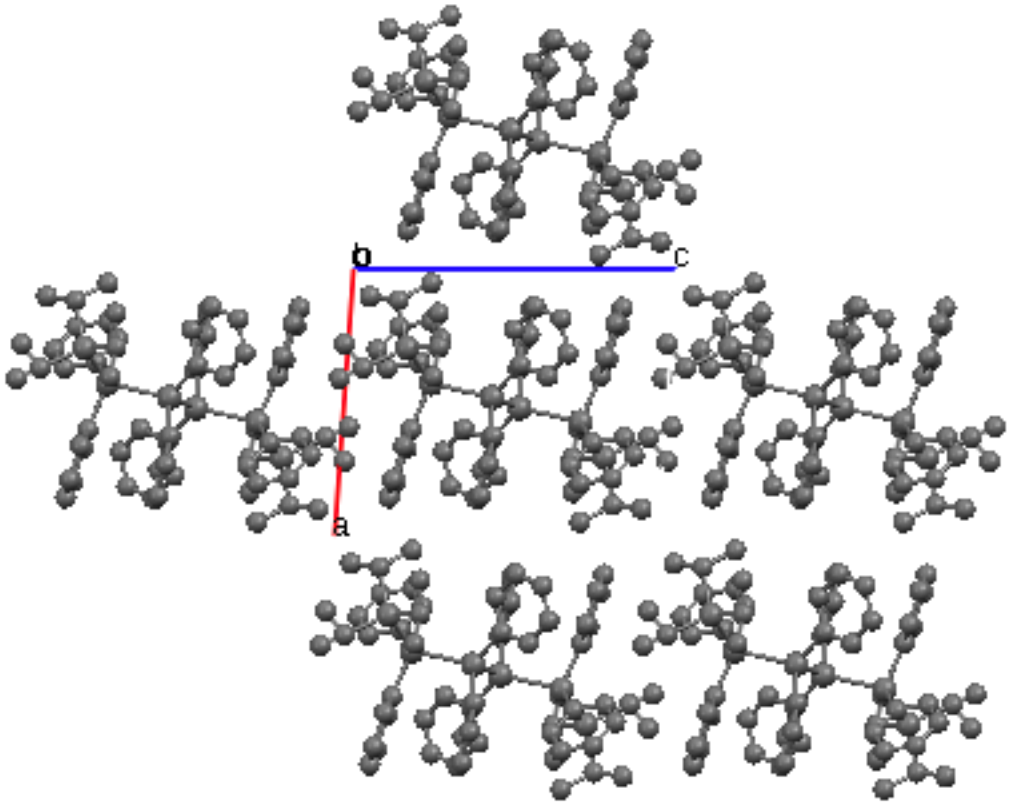
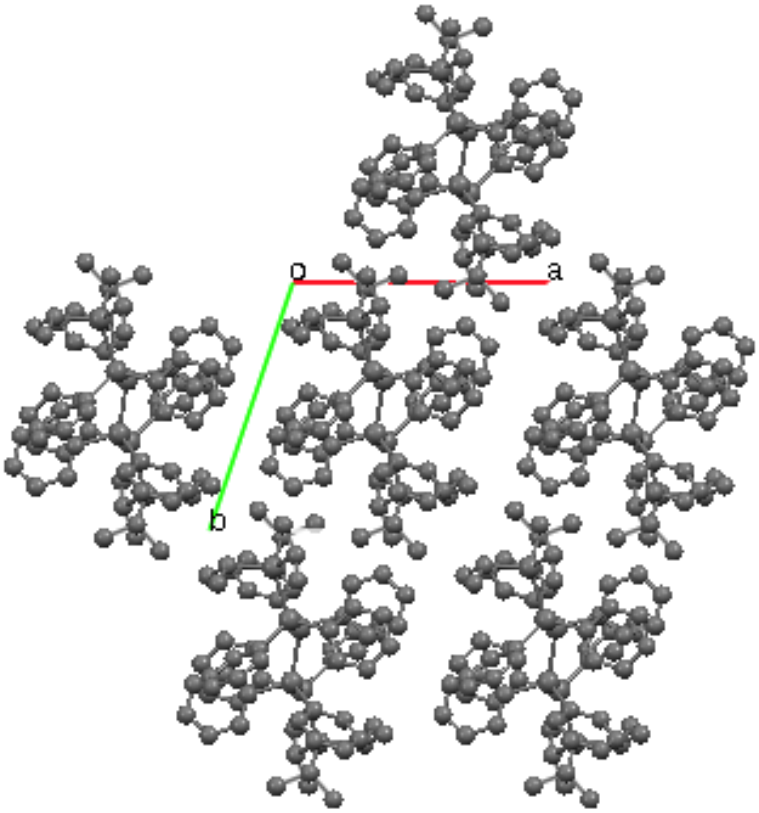
H(24A)	9478	8644	4485	28
H(25A)	8721	9379	3070	28
H(26A)	6533	8758	2612	23
H(27A)	5101	7378	3555	17
H(29A)	2377	4933	5664	22
H(30A)	600	5623	5801	31
H(31A)	788	7684	5615	38
H(32A)	2753	9075	5328	34
H(33A)	4547	8408	5208	23

Packing of 1 along the crystallographic *a*-axis



This journal is © The Royal Society of Chemistry 2013

Packing of 1 along the crystallographic *b*-axis



Packing of 1 along the crystallographic *c*-axis