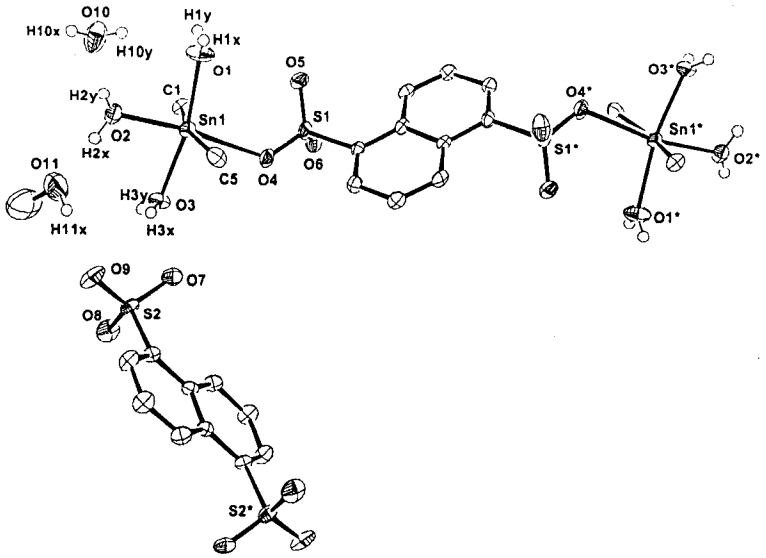


Figure S1: ORTEP diagram of **4**.

Table S1: Selected bond distances (Å) and angles (°) for **4**

Bond distances			
Sn1-O1	2.248(10)	Sn1-O4	2.515(57)
Sn1-O2	2.163(57)	Sn1-C1	2.108(80)
Sn1-O3	2.199(15)	Sn1-C5	2.108(21)
Bond angles			
C1-Sn1-C5	162.25(15)	C1-Sn1-O3	92.62(12)
O1-Sn1-O3	167.62(11)	C5-Sn1-O1	91.97(15)
O2-Sn1-O4	171.73(9)	C5-Sn1-O3	89.11(15)
O1-Sn1-O2	83.37(11)	C5-Sn1-O2	99.61(15)
O1-Sn1-O4	104.86(11)	C5-Sn1-O4	79.65(14)
C1-Sn1-O2	98.13(13)	O2-Sn1-O3	84.29(11)
C1-Sn1-O4	82.78(12)	O4-Sn1-O3	87.47(11)
C1-Sn1-O1	90.10(12)	S1-O4-Sn1	127.89(15)

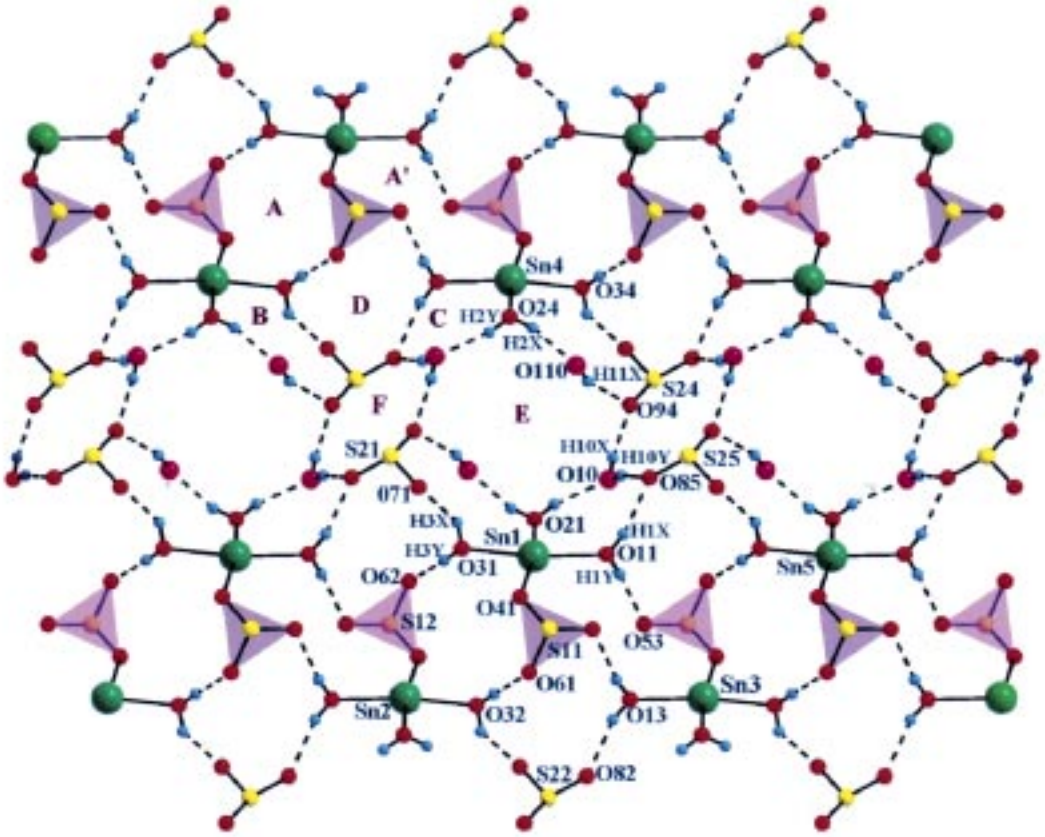


Figure S2: The two-dimensional layer of **4**

Table **S2**: Hydrogen bonding parameters in **4**

Bond	Distances (Å)			angle(°)	Symmetry
	O-H	O---O	H---O	O-H---O	
O11-H1x---O82	0.820(51)	2.689(50)	1.896(56)	162.48(41)	1+x, y, z
O11-H1y---O53	0.827(68)	2.677(46)	1.855(71)	171.59(54)	2-x,2-y,2-z
O24-H2x---O110	0.821(36)	2.587(83)	1.789(71)	163.67(36)	x,y,z
O21-H2y---O10	0.820(54)	2.665(58)	1.864(62)	165.30(48)	x,y,z
O31-H3x---O71	0.805(33)	2.668(47)	2.078(47)	130.1(28)	x,y,z
O31-H3y---O62	0.819(65)	2.642(52)	1.83(74)	171.66(61)	1-x,2-y,2-z
O10-H10x---O94	0.828(45)	2.822(86)	1.998(72)	171.53(40)	1-x,1-y,1-z
O10-H10y---O85	0.817(62)	2.805(61)	2.00(7)	168.34(54)	1+x,y,z
O110-H11x---O94	0.831(14)	2.831(48)	2.028(34)	162.32(36)	x,y,z

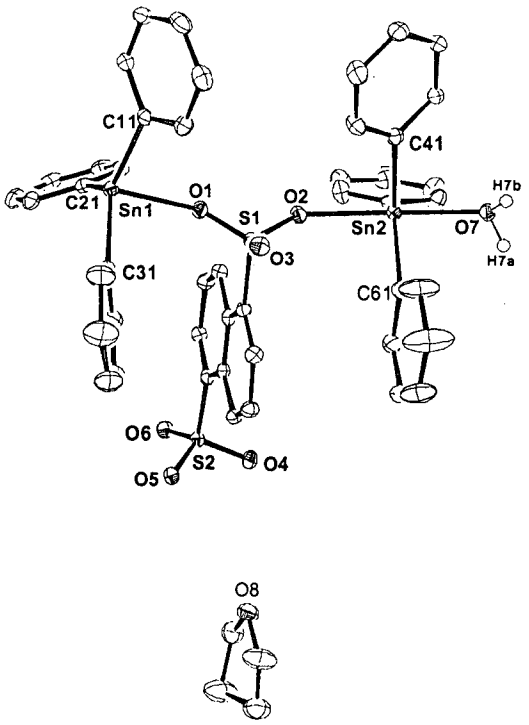


Figure S3: ORTEP Diagram of **5**

Table S3: Selected bond distances (Å) and angles (°) for **5**

Bond distances			
Sn1-O1	2.324(2)	Sn2-O2	2.298(1)
Sn1-O5	2.236(1)	Sn1-O7	2.233(1)
Sn1-C11	2.112(2)	Sn1-C41	2.128(2)
Sn1-C21	2.120(2)	Sn1-C51	2.140(2)
Sn1-C31	2.116(2)	Sn1-C11	2.125(2)
Bond Angles			
O1-Sn1-O5	175.97(5)	O2-Sn1-O7	176.83(5)
C11-Sn1-C21	123.29(7)	C41-Sn1-C51	115.88(7)
C11-Sn1-C31	119.15(7)	C41-Sn1-C61	116.08(7)
C21-Sn1-C31	117.48(7)	C51-Sn1-C61	128.00(7)

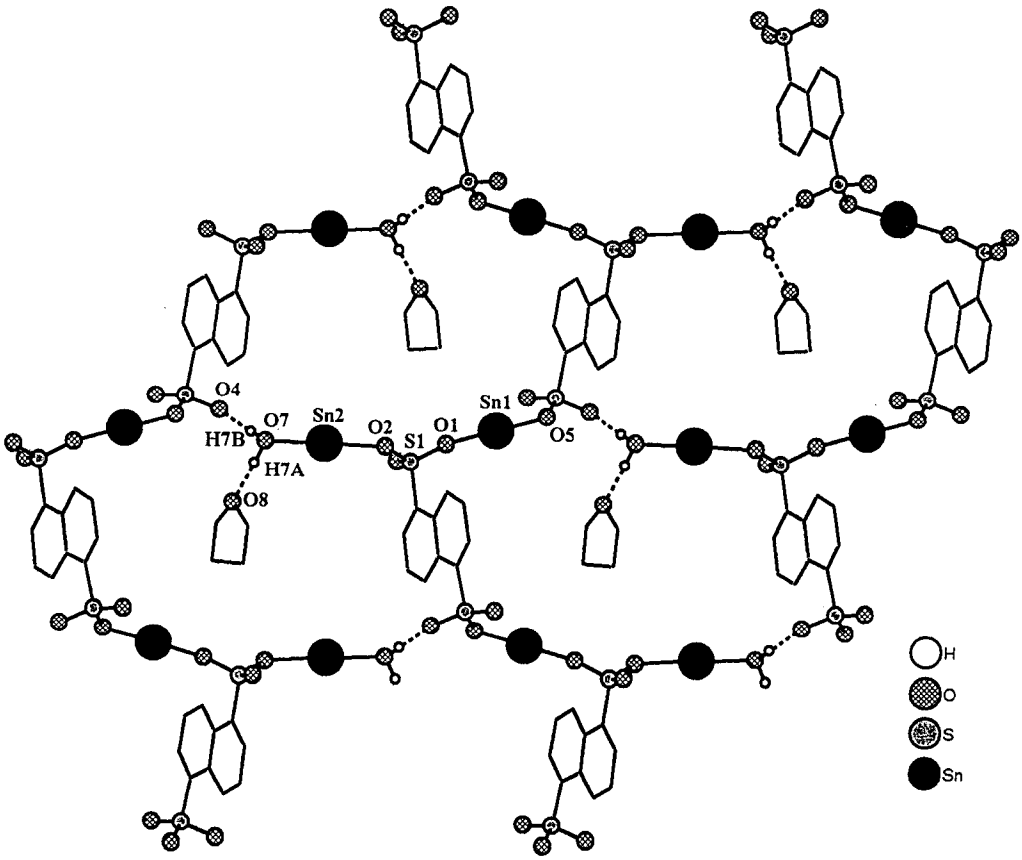
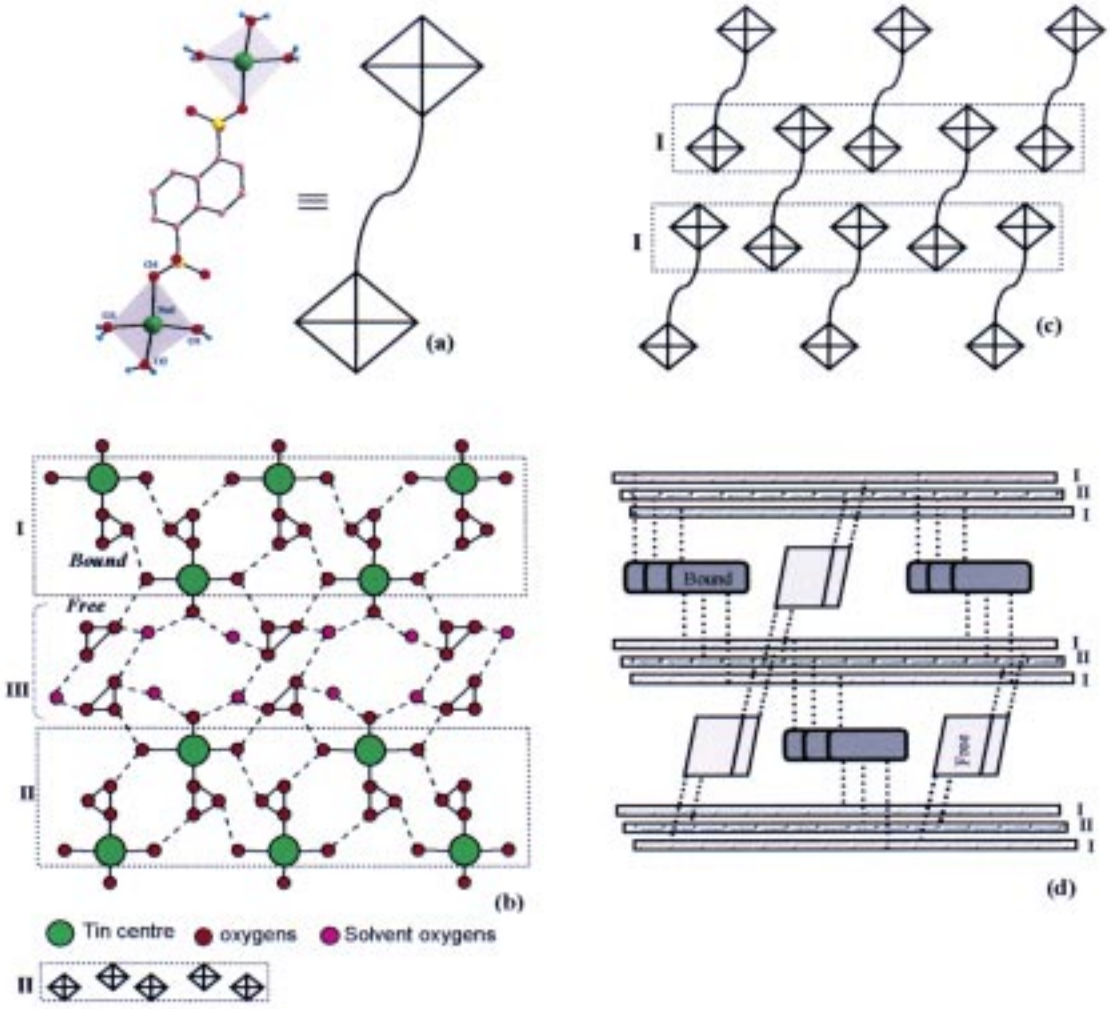


Figure **S4:** 2D-Layered Structure of **5**

Table S4: Hydrogen bonding parameters in **5**

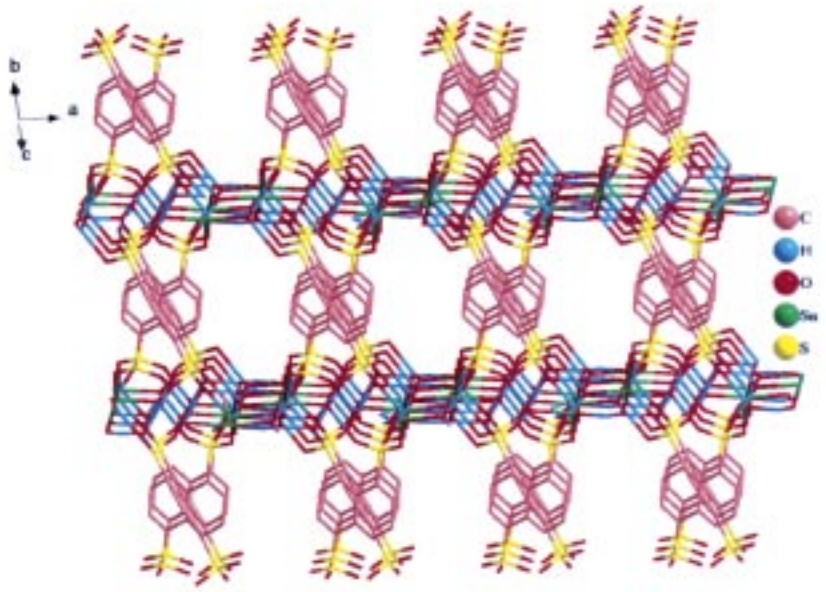
Bond	Distances (Å)			Angle(°)	Symmetry
	O-H	O---O	H---O	O-H---O	
O7-H7B---O4	0.856(32)	2.613(2)	1.763(33)	171.98(35)	2-x,0.5+y,0.5-z
O11-H1y---O53	0.908(29)	2.618(2)	1.711(29)	176.68(27)	2-x,0.5+y,0.5-z

Schematic picture showing the stepwise construction of pillared 3-D network in 4

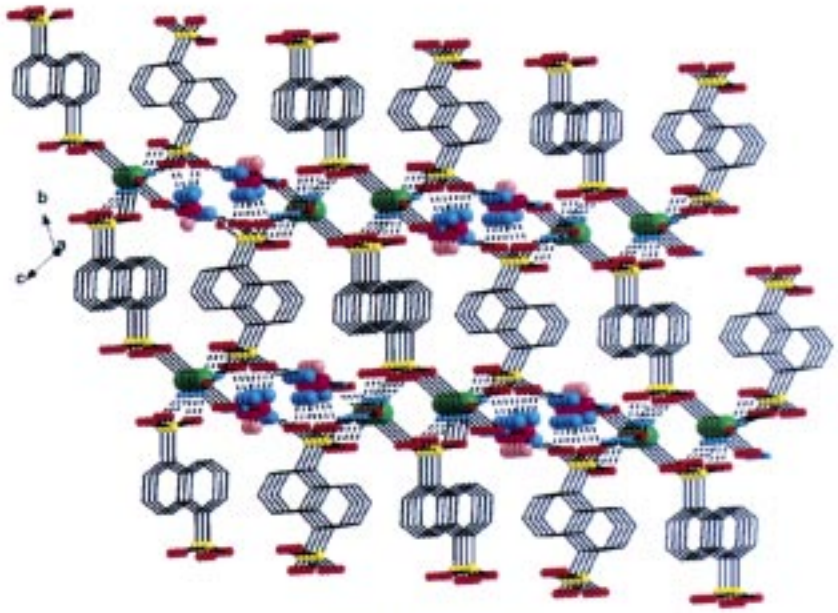


Caption for the Scheme: (a) The cationic ditin motif is shown in the cartoon as two kites attached by a string. The string is 1,5-naphthalene disulfonate. Note that the kite is not perfectly planar. The centre of the kite is a tin and the corners are three oxygens from water molecules of coordination and one oxygen from the coordinated sulfonate. (b) The layered structure showing the connection between segments I and II in a given sheet through the segment III. The triangles with red corners represent the sulfonates. The sulfur is not shown and the red centers are the oxygens. *Bound* and *free* represent the coordinated and anionic sulfonates respectively. (c) Relative disposition of the ditin units in segments of two different sheets. (d) A cartoon of the pillaring between different sheets.

3D-Pillared Structure of 4



View along ab-plane



View along a-axis

Table 5: Crystal data and structure refinement for 4

Identification code	vc92	
Empirical formula	C38 H72 O22 S4 Sn2	
Formula weight	1246.58	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.093(3) Å	α= 113.35(4)°.
	b = 11.484(4) Å	β= 94.59(4)°.
	c = 14.058(4) Å	γ = 100.65(4)°.
Volume	1305.3(7) $Å^3$	
Z	1	
Density (calculated)	1.586 Mg/m^3	
Absorption coefficient	1.191 mm^{-1}	
F(000)	640	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Theta range for data collection	1.96 to 24.16°.	
Index ranges	$-10 \le h \le 10, -13 \le k \le 12, -16 \le l \le 16$	
Reflections collected	8257	
Independent reflections	3847 [R(int) = 0.0460]	
Completeness to theta = 24.16°	91.7 %	
Absorption correction	Not applied	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3847 / 34 / 327	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0886	
R indices (all data)	R1 = 0.0378, wR2 = 0.0906	
Largest diff. peak and hole	1.307 and -1.240 $e.Å^{-3}$	

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6806(4)	8807(3)	9827(3)	22(1)
C(2)	6462(5)	7484(4)	9900(3)	24(1)
C(3)	6831(5)	7662(4)	11021(3)	35(1)
C(4)	6486(6)	6385(5)	11151(4)	44(1)
C(5)	6664(5)	9313(4)	7049(3)	32(1)
C(6)	6168(5)	8229(4)	5954(3)	37(1)
C(7)	5938(6)	8754(6)	5142(4)	54(2)
C(8)	5327(10)	7747(7)	4046(4)	90(2)
C(9)	8598(4)	13410(3)	9627(3)	18(1)
C(10)	7720(4)	13306(3)	8756(3)	21(1)
C(11)	8047(4)	14271(3)	8372(3)	23(1)
C(12)	9849(4)	14512(3)	10203(3)	16(1)
C(13)	10762(4)	14683(3)	11134(3)	21(1)
C(14)	744(4)	8580(3)	5019(3)	18(1)
C(15)	636(5)	7828(4)	3973(3)	27(1)
C(16)	55(5)	8238(4)	3233(3)	27(1)
C(17)	291(4)	9801(3)	5387(3)	18(1)
C(18)	399(4)	10618(4)	6461(3)	24(1)
C(19)	2319(9)	4896(8)	6549(7)	91(2)
O(1)	9055(3)	8524(3)	8264(2)	37(1)
O(2)	6096(3)	6647(2)	7422(2)	29(1)
O(3)	4176(3)	8507(3)	8123(2)	28(1)
O(4)	6893(3)	11158(2)	9285(2)	29(1)
O(5)	9521(3)	11621(3)	10059(2)	31(1)
O(6)	7777(3)	12712(3)	11086(2)	32(1)
O(7)	2656(3)	8967(3)	6656(2)	32(1)
O(8)	100(3)	7737(3)	6430(2)	35(1)
O(9)	1829(4)	6768(3)	5310(2)	38(1)
O(10)	8216(5)	5535(3)	6472(3)	49(1)
O(11)	3450(5)	5511(4)	6255(4)	79(2)
S(1)	8167(1)	12126(1)	10050(1)	20(1)

S(2)	1389(1)	7970(1)	5922(1)	22(1)
Sn(1)	6652(1)	8745(1)	8303(1)	18(1)

Table 7. Bond lengths [Å] and angles [°] for 4.

C(1)-C(2)	1.539(5)
C(1)-Sn(1)	2.107(4)
C(2)-C(3)	1.508(5)
C(3)-C(4)	1.528(6)
C(5)-C(6)	1.512(6)
C(5)-Sn(1)	2.108(4)
C(6)-C(7)	1.505(6)
C(7)-C(8)	1.494(8)
C(9)-C(10)	1.358(5)
C(9)-C(12)	1.435(5)
C(9)-S(1)	1.789(3)
C(10)-C(11)	1.408(5)
C(11)-C(13)#1	1.355(5)
C(12)-C(13)	1.415(5)
C(12)-C(12)#1	1.441(6)
C(13)-C(11)#1	1.355(5)
C(14)-C(15)	1.363(5)
C(14)-C(17)	1.440(5)
C(14)-S(2)	1.784(3)
C(15)-C(16)	1.406(5)
C(16)-C(18)#2	1.364(6)
C(17)-C(18)	1.411(5)
C(17)-C(17)#2	1.437(6)
C(18)-C(16)#2	1.364(6)
C(19)-O(11)	1.326(8)
O(1)-Sn(1)	2.249(3)
O(2)-Sn(1)	2.163(3)
O(3)-Sn(1)	2.198(3)
O(4)-S(1)	1.453(3)
O(4)-Sn(1)	2.515(3)
O(5)-S(1)	1.456(3)
O(6)-S(1)	1.448(3)
O(7)-S(2)	1.445(3)
O(8)-S(2)	1.458(3)

O(9)-S(2)	1.457(3)
C(2)-C(1)-Sn(1)	116.6(2)
C(3)-C(2)-C(1)	111.0(3)
C(2)-C(3)-C(4)	113.6(3)
C(6)-C(5)-Sn(1)	116.4(3)
C(7)-C(6)-C(5)	111.7(4)
C(8)-C(7)-C(6)	115.3(5)
C(10)-C(9)-C(12)	121.7(3)
C(10)-C(9)-S(1)	118.4(3)
C(12)-C(9)-S(1)	120.0(3)
C(9)-C(10)-C(11)	120.4(3)
C(13)#1-C(11)-C(10)	120.6(3)
C(13)-C(12)-C(9)	123.6(3)
C(13)-C(12)-C(12)#1	119.6(4)
C(9)-C(12)-C(12)#1	116.7(4)
C(11)#1-C(13)-C(12)	120.9(3)
C(15)-C(14)-C(17)	121.4(3)
C(15)-C(14)-S(2)	117.7(3)
C(17)-C(14)-S(2)	120.8(3)
C(14)-C(15)-C(16)	119.6(4)
C(18)#2-C(16)-C(15)	121.3(4)
C(18)-C(17)-C(17)#2	118.8(4)
C(18)-C(17)-C(14)	123.3(3)
C(17)#2-C(17)-C(14)	117.8(4)
C(16)#2-C(18)-C(17)	121.0(3)
S(1)-O(4)-Sn(1)	127.91(16)
O(6)-S(1)-O(4)	112.35(17)
O(6)-S(1)-O(5)	112.60(18)
O(4)-S(1)-O(5)	112.24(17)
O(6)-S(1)-C(9)	106.15(17)
O(4)-S(1)-C(9)	105.93(15)
O(5)-S(1)-C(9)	106.99(17)
O(7)-S(2)-O(9)	112.24(19)
O(7)-S(2)-O(8)	112.27(19)
O(9)-S(2)-O(8)	112.06(19)

O(7)-S(2)-C(14)	106.96(16)
O(9)-S(2)-C(14)	107.16(17)
O(8)-S(2)-C(14)	105.64(17)
C(1)-Sn(1)-C(5)	162.24(16)
C(1)-Sn(1)-O(2)	98.13(13)
C(5)-Sn(1)-O(2)	99.63(15)
C(1)-Sn(1)-O(3)	92.61(14)
C(5)-Sn(1)-O(3)	89.11(14)
O(2)-Sn(1)-O(3)	84.29(13)
C(1)-Sn(1)-O(1)	90.12(14)
C(5)-Sn(1)-O(1)	91.97(15)
O(2)-Sn(1)-O(1)	83.35(13)
O(3)-Sn(1)-O(1)	167.60(12)
C(1)-Sn(1)-O(4)	82.77(12)
C(5)-Sn(1)-O(4)	79.65(14)
O(2)-Sn(1)-O(4)	171.75(10)
O(3)-Sn(1)-O(4)	87.48(11)
O(1)-Sn(1)-O(4)	104.87(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+3,-z+2 #2 -x,-y+2,-z+1

Table 8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 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)	29(2)	24(2)	17(2)	10(2)	7(2)	11(2)
C(2)	32(2)	24(2)	20(2)	14(2)	4(2)	7(2)
C(3)	51(3)	35(2)	24(2)	19(2)	-1(2)	6(2)
C(4)	62(3)	49(3)	37(2)	33(2)	10(2)	16(2)
C(5)	27(2)	42(2)	33(2)	28(2)	1(2)	-2(2)
C(6)	44(3)	52(3)	27(2)	24(2)	11(2)	25(2)
C(7)	54(3)	80(4)	36(3)	40(3)	3(2)	1(3)
C(8)	143(7)	106(5)	29(3)	29(3)	7(4)	52(5)
C(9)	21(2)	16(2)	20(2)	10(2)	7(2)	5(2)
C(10)	24(2)	19(2)	21(2)	10(2)	4(2)	5(2)
C(11)	29(2)	23(2)	16(2)	7(2)	0(2)	8(2)
C(12)	20(2)	17(2)	17(2)	9(2)	9(2)	8(2)
C(13)	27(2)	24(2)	21(2)	17(2)	8(2)	10(2)
C(14)	21(2)	23(2)	16(2)	11(2)	6(2)	9(2)
C(15)	35(2)	24(2)	27(2)	13(2)	7(2)	13(2)
C(16)	39(2)	30(2)	16(2)	10(2)	7(2)	13(2)
C(17)	17(2)	25(2)	18(2)	14(2)	3(2)	4(2)
C(18)	28(2)	30(2)	17(2)	14(2)	3(2)	9(2)
C(19)	86(5)	102(6)	122(7)	80(5)	24(5)	32(4)
O(1)	24(2)	64(2)	28(2)	20(2)	10(1)	22(2)
O(2)	36(2)	22(1)	28(2)	10(1)	2(1)	6(1)
O(3)	19(1)	45(2)	31(2)	27(1)	6(1)	7(1)
O(4)	36(2)	19(1)	34(2)	17(1)	0(1)	2(1)
O(5)	30(2)	32(1)	43(2)	26(1)	6(1)	11(1)
O(6)	41(2)	32(1)	26(2)	16(1)	14(1)	-1(1)
O(7)	32(2)	35(2)	34(2)	19(1)	-6(1)	10(1)
O(8)	40(2)	44(2)	36(2)	30(1)	15(1)	13(1)
O(9)	57(2)	35(2)	34(2)	19(1)	9(2)	29(2)
O(10)	69(2)	33(2)	49(2)	15(2)	30(2)	15(2)
O(11)	66(3)	56(2)	104(4)	43(2)	-34(3)	-9(2)
S(1)	24(1)	18(1)	23(1)	14(1)	4(1)	3(1)

S(2)	29(1)	25(1)	22(1)	16(1)	7(1)	12(1)
Sn(1)	20(1)	22(1)	17(1)	14(1)	5(1)	7(1)

Table 9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4.

	x	y	z	U(eq)
H(1A)	7835	9284	10207	27
H(1B)	6104	9312	10192	27
H(2A)	5385	7054	9627	29
H(2B)	7063	6922	9465	29
H(3A)	6247	8245	11453	43
H(3B)	7911	8085	11284	43
H(4A)	5412	5974	10917	65
H(4B)	6759	6565	11885	65
H(4C)	7070	5804	10733	65
H(5A)	5999	9919	7146	38
H(5B)	7695	9796	7096	38
H(6A)	6940	7719	5789	44
H(6B)	5218	7645	5929	44
H(7A)	5239	9331	5353	65
H(7B)	6913	9287	5141	65
H(8A)	6025	7186	3817	135
H(8B)	5214	8174	3581	135
H(8C)	4347	7227	4030	135
H(10)	6889	12586	8406	25
H(11)	7433	14188	7767	27
H(13)	10540	14062	11413	25
H(15)	948	7039	3748	33
H(16)	-22	7713	2512	33
H(18)	789	10371	6974	28
H(19A)	2723	4691	7108	136
H(19B)	1786	4094	5954	136
H(19C)	1622	5451	6799	136
H(1X)	9540(60)	8400(70)	7780(30)	84(8)
H(1Y)	9530(60)	8420(60)	8740(40)	84(8)
H(2X)	5200(30)	6300(60)	7160(50)	84(8)

H(2Y)	6620(50)	6200(50)	7060(40)	84(8)
H(3X)	3890(70)	8230(60)	7500(20)	84(8)
H(3Y)	3550(60)	8200(60)	8400(40)	84(8)
H(10X)	8130(80)	4840(40)	5950(30)	84(8)
H(10Y)	8760(70)	6110(40)	6370(50)	84(8)
H(11x)	3101	5838	5882	118

Table 10: Crystal data and structure refinement for 5

Identification code	vc88a	
Empirical formula	C50 H46 O8 S2 Sn2	
Formula weight	1076.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.3593(6) Å	α= 90°.
	b = 15.9365(7) Å	β= 107.4430(10)°.
	c = 20.5615(9) Å	γ = 90°.
Volume	4488.9(3) $Å^3$	
Z	4	
Density (calculated)	1.593 Mg/m^3	
Absorption coefficient	1.261 mm^{-1}	
F(000)	2168	
Crystal size	0.2 x 0.1 x 0.3 mm^3	
Theta range for data collection	1.49 to 28.30°.	
Index ranges	$-16 \le h \le 18, -15 \le k \le 20, -26 \le l \le 26$	
Reflections collected	27492	
Independent reflections	10292 [R(int) = 0.0220]	
Completeness to theta = 28.30°	92.0 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000 and 0.822	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10292 / 0 / 743	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0623	
R indices (all data)	R1 = 0.0280, wR2 = 0.0640	
Largest diff. peak and hole	1.449 and -0.465 $e.Å^{-3}$	

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	5411(1)	7678(1)	3166(1)	14(1)
Sn(2)	10051(1)	7351(1)	2912(1)	14(1)
S(1)	7723(1)	6927(1)	3107(1)	14(1)
S(2)	6210(1)	3465(1)	1026(1)	14(1)
O(1)	6770(1)	7345(1)	2825(1)	18(1)
O(2)	8402(1)	7281(1)	2762(1)	18(1)
O(3)	8094(1)	6947(1)	3839(1)	20(1)
O(4)	7127(1)	3132(1)	962(1)	18(1)
O(5)	5955(1)	3013(1)	1584(1)	17(1)
O(6)	5422(1)	3479(1)	399(1)	19(1)
O(7)	11639(1)	7388(1)	3001(1)	18(1)
O(8)	7508(1)	967(1)	2113(1)	28(1)
C(1)	7552(1)	5858(1)	2852(1)	15(1)
C(2)	7892(1)	5268(1)	3350(1)	18(1)
C(3)	7786(1)	4412(1)	3182(1)	19(1)
C(4)	7326(1)	4159(1)	2529(1)	17(1)
C(5)	6953(1)	4754(1)	1998(1)	14(1)
C(6)	7078(1)	5630(1)	2153(1)	14(1)
C(7)	6737(1)	6230(1)	1625(1)	17(1)
C(8)	6288(1)	5983(1)	969(1)	19(1)
C(9)	6138(1)	5126(1)	809(1)	17(1)
C(10)	6452(1)	4526(1)	1305(1)	14(1)
C(11)	6121(1)	8779(1)	3636(1)	16(1)
C(12)	5714(1)	9569(1)	3436(1)	21(1)
C(13)	6115(2)	10283(1)	3805(1)	27(1)
C(14)	6921(2)	10210(1)	4373(1)	28(1)
C(15)	7341(2)	9433(2)	4573(1)	26(1)
C(16)	6945(1)	8717(1)	4204(1)	21(1)
C(21)	4576(1)	7618(1)	2124(1)	16(1)
C(22)	4978(2)	7833(1)	1601(1)	20(1)
C(23)	4419(2)	7773(1)	918(1)	24(1)

C(24)	3456(2)	7514(1)	748(1)	25(1)
C(25)	3050(2)	7297(1)	1261(1)	24(1)
C(26)	3608(2)	7345(1)	1941(1)	19(1)
C(31)	5591(1)	6554(1)	3738(1)	18(1)
C(32)	5578(2)	5785(1)	3414(1)	24(1)
C(33)	5744(2)	5040(1)	3784(1)	32(1)
C(34)	5918(2)	5062(2)	4481(1)	40(1)
C(35)	5909(2)	5822(2)	4810(1)	45(1)
C(36)	5752(2)	6564(1)	4438(1)	31(1)
C(41)	10151(1)	8535(1)	3406(1)	16(1)
C(42)	10768(1)	9148(1)	3275(1)	18(1)
C(43)	10845(1)	9938(1)	3578(1)	21(1)
C(44)	10303(2)	10124(1)	4015(1)	23(1)
C(45)	9688(2)	9520(1)	4152(1)	25(1)
C(46)	9612(2)	8731(1)	3850(1)	21(1)
C(51)	9713(1)	7386(1)	1826(1)	17(1)
C(52)	8757(2)	7490(2)	1411(1)	26(1)
C(53)	8546(2)	7589(2)	710(1)	30(1)
C(54)	9280(2)	7592(1)	408(1)	26(1)
C(55)	10239(2)	7494(2)	811(1)	29(1)
C(56)	10457(2)	7394(1)	1515(1)	24(1)
C(61)	10349(1)	6282(1)	3560(1)	18(1)
C(62)	10182(2)	5460(1)	3331(1)	23(1)
C(63)	10456(2)	4786(1)	3782(1)	28(1)
C(64)	10904(2)	4933(2)	4463(1)	42(1)
C(65)	11093(3)	5747(2)	4697(1)	66(1)
C(66)	10815(2)	6415(2)	4249(1)	45(1)
C(71)	7057(2)	471(2)	1513(1)	34(1)
C(72)	6954(3)	-398(2)	1785(2)	56(1)
C(73)	7797(2)	-456(2)	2426(1)	40(1)
C(74)	7900(3)	413(2)	2690(1)	45(1)

Table 12. Bond lengths [Å] and angles [°] for 5.

Sn(1)-C(11)	2.1120(18)
Sn(1)-C(31)	2.1164(19)
Sn(1)-C(21)	2.1199(19)
Sn(1)-O(5)#1	2.2364(13)
Sn(1)-O(1)	2.3244(13)
Sn(2)-C(61)	2.1252(19)
Sn(2)-C(41)	2.1279(18)
Sn(2)-C(51)	2.1405(19)
Sn(2)-O(7)	2.2327(14)
Sn(2)-O(2)	2.2978(13)
S(1)-O(3)	1.4380(13)
S(1)-O(1)	1.4754(14)
S(1)-O(2)	1.4790(14)
S(1)-C(1)	1.7773(18)
S(2)-O(6)	1.4386(13)
S(2)-O(4)	1.4608(13)
S(2)-O(5)	1.4905(13)
S(2)-C(10)	1.7866(18)
O(5)-Sn(1)#2	2.2364(13)
O(8)-C(71)	1.444(3)
O(8)-C(74)	1.450(3)
C(1)-C(2)	1.368(3)
C(1)-C(6)	1.440(2)
C(2)-C(3)	1.405(3)
C(3)-C(4)	1.366(3)
C(4)-C(5)	1.426(3)
C(5)-C(6)	1.431(3)
C(5)-C(10)	1.437(2)
C(6)-C(7)	1.418(3)
C(7)-C(8)	1.368(3)
C(8)-C(9)	1.405(3)
C(9)-C(10)	1.374(3)
C(11)-C(16)	1.396(3)
C(11)-C(12)	1.397(3)

C(12)-C(13)	1.392(3)
C(13)-C(14)	1.381(3)
C(14)-C(15)	1.385(3)
C(15)-C(16)	1.393(3)
C(21)-C(26)	1.396(3)
C(21)-C(22)	1.407(3)
C(22)-C(23)	1.395(3)
C(23)-C(24)	1.383(3)
C(24)-C(25)	1.393(3)
C(25)-C(26)	1.391(3)
C(31)-C(36)	1.387(3)
C(31)-C(32)	1.392(3)
C(32)-C(33)	1.391(3)
C(33)-C(34)	1.379(4)
C(34)-C(35)	1.388(4)
C(35)-C(36)	1.390(3)
C(41)-C(46)	1.398(3)
C(41)-C(42)	1.398(3)
C(42)-C(43)	1.394(3)
C(43)-C(44)	1.387(3)
C(44)-C(45)	1.390(3)
C(45)-C(46)	1.391(3)
C(51)-C(52)	1.392(3)
C(51)-C(56)	1.399(3)
C(52)-C(53)	1.391(3)
C(53)-C(54)	1.374(3)
C(54)-C(55)	1.387(3)
C(55)-C(56)	1.395(3)
C(61)-C(62)	1.388(3)
C(61)-C(66)	1.389(3)
C(62)-C(63)	1.397(3)
C(63)-C(64)	1.375(4)
C(64)-C(65)	1.382(4)
C(65)-C(66)	1.386(4)
C(71)-C(72)	1.518(4)
C(72)-C(73)	1.501(4)

C(73)-C(74)	1.478(4)
C(11)-Sn(1)-C(31)	119.16(7)
C(11)-Sn(1)-C(21)	123.29(7)
C(31)-Sn(1)-C(21)	117.47(7)
C(11)-Sn(1)-O(5)#1	91.87(6)
C(31)-Sn(1)-O(5)#1	92.51(6)
C(21)-Sn(1)-O(5)#1	88.49(6)
C(11)-Sn(1)-O(1)	89.64(6)
C(31)-Sn(1)-O(1)	90.01(6)
C(21)-Sn(1)-O(1)	87.56(6)
O(5)#1-Sn(1)-O(1)	175.97(5)
C(61)-Sn(2)-C(41)	116.08(7)
C(61)-Sn(2)-C(51)	128.00(7)
C(41)-Sn(2)-C(51)	115.88(7)
C(61)-Sn(2)-O(7)	87.78(6)
C(41)-Sn(2)-O(7)	90.96(6)
C(51)-Sn(2)-O(7)	89.49(7)
C(61)-Sn(2)-O(2)	92.95(6)
C(41)-Sn(2)-O(2)	91.49(6)
C(51)-Sn(2)-O(2)	87.63(6)
O(7)-Sn(2)-O(2)	176.83(5)
O(3)-S(1)-O(1)	114.21(8)
O(3)-S(1)-O(2)	113.76(8)
O(1)-S(1)-O(2)	107.78(8)
O(3)-S(1)-C(1)	107.77(9)
O(1)-S(1)-C(1)	106.67(8)
O(2)-S(1)-C(1)	106.11(8)
O(6)-S(2)-O(4)	114.44(8)
O(6)-S(2)-O(5)	112.85(8)
O(4)-S(2)-O(5)	109.27(8)
O(6)-S(2)-C(10)	107.36(8)
O(4)-S(2)-C(10)	106.21(8)
O(5)-S(2)-C(10)	106.14(8)
S(1)-O(1)-Sn(1)	138.45(8)
S(1)-O(2)-Sn(2)	139.00(8)

S(2)-O(5)-Sn(1)#2	136.69(8)
C(71)-O(8)-C(74)	109.30(18)
C(2)-C(1)-C(6)	122.00(17)
C(2)-C(1)-S(1)	116.80(14)
C(6)-C(1)-S(1)	121.21(14)
C(1)-C(2)-C(3)	119.66(17)
C(4)-C(3)-C(2)	120.89(18)
C(3)-C(4)-C(5)	121.08(18)
C(4)-C(5)-C(6)	119.01(16)
C(4)-C(5)-C(10)	123.54(17)
C(6)-C(5)-C(10)	117.45(16)
C(7)-C(6)-C(5)	119.63(16)
C(7)-C(6)-C(1)	123.05(17)
C(5)-C(6)-C(1)	117.32(16)
C(8)-C(7)-C(6)	120.90(18)
C(7)-C(8)-C(9)	120.35(18)
C(10)-C(9)-C(8)	120.58(17)
C(9)-C(10)-C(5)	121.04(17)
C(9)-C(10)-S(2)	115.55(14)
C(5)-C(10)-S(2)	123.40(14)
C(16)-C(11)-C(12)	119.02(18)
C(16)-C(11)-Sn(1)	119.75(14)
C(12)-C(11)-Sn(1)	120.82(14)
C(13)-C(12)-C(11)	120.52(19)
C(14)-C(13)-C(12)	119.8(2)
C(13)-C(14)-C(15)	120.4(2)
C(14)-C(15)-C(16)	120.0(2)
C(15)-C(16)-C(11)	120.22(19)
C(26)-C(21)-C(22)	118.26(18)
C(26)-C(21)-Sn(1)	120.15(14)
C(22)-C(21)-Sn(1)	121.58(14)
C(23)-C(22)-C(21)	120.51(19)
C(24)-C(23)-C(22)	120.4(2)
C(23)-C(24)-C(25)	119.71(19)
C(26)-C(25)-C(24)	120.2(2)
C(25)-C(26)-C(21)	120.98(19)

C(36)-C(31)-C(32)	118.73(19)
C(36)-C(31)-Sn(1)	121.40(15)
C(32)-C(31)-Sn(1)	119.84(15)
C(33)-C(32)-C(31)	120.9(2)
C(34)-C(33)-C(32)	119.6(2)
C(33)-C(34)-C(35)	120.2(2)
C(34)-C(35)-C(36)	119.9(2)
C(31)-C(36)-C(35)	120.6(2)
C(46)-C(41)-C(42)	118.52(17)
C(46)-C(41)-Sn(2)	122.58(14)
C(42)-C(41)-Sn(2)	118.90(13)
C(43)-C(42)-C(41)	120.95(18)
C(44)-C(43)-C(42)	119.88(18)
C(43)-C(44)-C(45)	119.77(19)
C(44)-C(45)-C(46)	120.40(19)
C(45)-C(46)-C(41)	120.49(18)
C(52)-C(51)-C(56)	117.85(18)
C(52)-C(51)-Sn(2)	121.03(15)
C(56)-C(51)-Sn(2)	120.79(14)
C(53)-C(52)-C(51)	121.1(2)
C(54)-C(53)-C(52)	120.7(2)
C(53)-C(54)-C(55)	119.2(2)
C(54)-C(55)-C(56)	120.4(2)
C(55)-C(56)-C(51)	120.7(2)
C(62)-C(61)-C(66)	118.12(19)
C(62)-C(61)-Sn(2)	124.15(15)
C(66)-C(61)-Sn(2)	117.50(15)
C(61)-C(62)-C(63)	121.0(2)
C(64)-C(63)-C(62)	119.8(2)
C(63)-C(64)-C(65)	119.9(2)
C(64)-C(65)-C(66)	120.1(3)
C(65)-C(66)-C(61)	121.0(2)
O(8)-C(71)-C(72)	104.7(2)
C(73)-C(72)-C(71)	103.7(2)
C(74)-C(73)-C(72)	103.4(2)
O(8)-C(74)-C(73)	107.3(2)

Symmetry transformations used to generate equivalent atoms:

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

Table 13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 5. 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}
Sn(1)	14(1)	13(1)	14(1)	0(1)	4(1)	0(1)
Sn(2)	14(1)	13(1)	14(1)	-1(1)	4(1)	-1(1)
S(1)	13(1)	15(1)	15(1)	-3(1)	4(1)	-1(1)
S(2)	13(1)	16(1)	12(1)	-1(1)	3(1)	-1(1)
O(1)	15(1)	18(1)	20(1)	-2(1)	7(1)	1(1)
O(2)	16(1)	20(1)	21(1)	-1(1)	7(1)	-3(1)
O(3)	24(1)	20(1)	16(1)	-4(1)	4(1)	-2(1)
O(4)	17(1)	21(1)	16(1)	0(1)	6(1)	2(1)
O(5)	15(1)	19(1)	16(1)	-1(1)	4(1)	-2(1)
O(6)	18(1)	21(1)	17(1)	-2(1)	1(1)	-2(1)
O(7)	14(1)	19(1)	20(1)	-2(1)	4(1)	-1(1)
O(8)	31(1)	23(1)	31(1)	4(1)	9(1)	-3(1)
C(1)	14(1)	15(1)	17(1)	-3(1)	5(1)	-1(1)
C(2)	18(1)	21(1)	13(1)	-2(1)	2(1)	0(1)
C(3)	20(1)	18(1)	18(1)	2(1)	3(1)	2(1)
C(4)	17(1)	16(1)	18(1)	0(1)	6(1)	0(1)
C(5)	12(1)	17(1)	13(1)	-1(1)	5(1)	0(1)
C(6)	12(1)	17(1)	14(1)	0(1)	4(1)	0(1)
C(7)	17(1)	15(1)	19(1)	1(1)	5(1)	0(1)
C(8)	21(1)	19(1)	16(1)	4(1)	4(1)	2(1)
C(9)	17(1)	20(1)	14(1)	-1(1)	4(1)	-1(1)
C(10)	13(1)	16(1)	15(1)	-3(1)	5(1)	-1(1)
C(11)	17(1)	16(1)	19(1)	-3(1)	9(1)	-2(1)
C(12)	17(1)	19(1)	29(1)	2(1)	9(1)	-1(1)
C(13)	27(1)	16(1)	41(1)	-1(1)	17(1)	-3(1)
C(14)	31(1)	24(1)	34(1)	-12(1)	18(1)	-12(1)
C(15)	24(1)	32(1)	21(1)	-6(1)	8(1)	-7(1)
C(16)	20(1)	22(1)	19(1)	-1(1)	7(1)	1(1)
C(21)	20(1)	14(1)	17(1)	0(1)	7(1)	3(1)
C(22)	22(1)	17(1)	22(1)	1(1)	10(1)	1(1)
C(23)	38(1)	18(1)	20(1)	3(1)	13(1)	6(1)

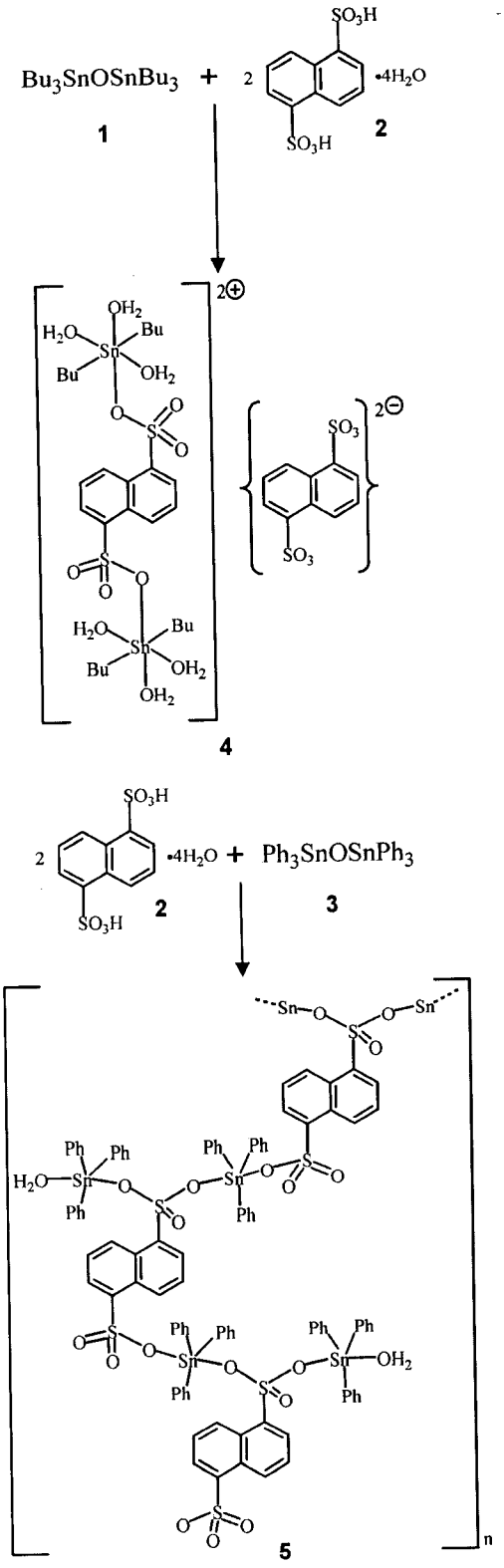
C(24)	33(1)	23(1)	15(1)	-2(1)	0(1)	10(1)
C(25)	19(1)	25(1)	25(1)	-6(1)	2(1)	4(1)
C(26)	19(1)	21(1)	20(1)	-3(1)	7(1)	3(1)
C(31)	16(1)	17(1)	23(1)	3(1)	7(1)	1(1)
C(32)	27(1)	19(1)	31(1)	0(1)	15(1)	-1(1)
C(33)	33(1)	16(1)	55(2)	4(1)	25(1)	0(1)
C(34)	44(1)	26(1)	50(2)	20(1)	15(1)	7(1)
C(35)	63(2)	38(1)	29(1)	14(1)	6(1)	2(1)
C(36)	44(1)	22(1)	24(1)	3(1)	7(1)	0(1)
C(41)	15(1)	15(1)	15(1)	-1(1)	3(1)	0(1)
C(42)	18(1)	18(1)	21(1)	0(1)	8(1)	0(1)
C(43)	21(1)	16(1)	25(1)	1(1)	7(1)	-3(1)
C(44)	24(1)	20(1)	22(1)	-7(1)	2(1)	-2(1)
C(45)	26(1)	30(1)	22(1)	-9(1)	11(1)	-4(1)
C(46)	23(1)	23(1)	19(1)	-4(1)	10(1)	-7(1)
C(51)	22(1)	14(1)	15(1)	-1(1)	4(1)	-2(1)
C(52)	20(1)	38(1)	20(1)	-1(1)	6(1)	-5(1)
C(53)	25(1)	38(1)	20(1)	0(1)	-3(1)	-7(1)
C(54)	37(1)	24(1)	15(1)	-1(1)	3(1)	4(1)
C(55)	31(1)	39(1)	20(1)	6(1)	12(1)	8(1)
C(56)	22(1)	32(1)	19(1)	5(1)	7(1)	7(1)
C(61)	19(1)	17(1)	20(1)	2(1)	9(1)	0(1)
C(62)	22(1)	20(1)	25(1)	-1(1)	3(1)	-1(1)
C(63)	28(1)	16(1)	40(1)	2(1)	11(1)	0(1)
C(64)	73(2)	23(1)	32(1)	12(1)	19(1)	10(1)
C(65)	140(3)	31(1)	17(1)	3(1)	9(2)	13(2)
C(66)	90(2)	19(1)	20(1)	-1(1)	8(1)	5(1)
C(71)	28(1)	32(1)	35(1)	3(1)	-1(1)	-4(1)
C(72)	58(2)	30(1)	57(2)	5(1)	-17(2)	-13(1)
C(73)	46(2)	30(1)	41(1)	9(1)	8(1)	0(1)
C(74)	73(2)	32(1)	28(1)	8(1)	12(1)	-6(1)

Table 14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 5.

	x	y	z	U(eq)
H(7A)	11921(19)	6885(18)	2970(13)	37(7)
H(7B)	12020(30)	7604(19)	3365(18)	52(9)
H(2)	8174(17)	5431(15)	3825(12)	27(6)
H(3)	8006(17)	3992(15)	3534(12)	25(6)
H(4)	7263(15)	3587(14)	2425(10)	14(5)
H(7)	6811(17)	6801(16)	1728(12)	27(6)
H(8)	6080(16)	6381(15)	614(12)	22(6)
H(9)	5807(16)	4965(14)	366(12)	19(6)
H(12)	5154(18)	9602(17)	3043(13)	30(7)
H(13)	5805(18)	10812(17)	3690(13)	33(7)
H(14)	7178(18)	10643(17)	4610(13)	34(7)
H(15)	7904(16)	9376(14)	4983(11)	18(5)
H(16)	7253(16)	8203(16)	4336(11)	23(6)
H(22)	5648(16)	8019(14)	1708(11)	14(5)
H(23)	4753(19)	7941(17)	551(14)	37(7)
H(24)	3100(20)	7473(16)	298(15)	32(7)
H(25)	2404(17)	7103(14)	1139(11)	19(5)
H(26)	3342(17)	7204(14)	2285(12)	21(6)
H(32)	5458(18)	5743(16)	2940(13)	29(6)
H(33)	5760(20)	4506(18)	3551(14)	42(8)
H(34)	6040(20)	4580(20)	4756(16)	58(9)
H(35)	6040(20)	5840(20)	5270(17)	59(9)
H(36)	5762(19)	7098(17)	4672(13)	34(7)
H(42)	11136(16)	9047(14)	2978(11)	19(5)
H(43)	11265(17)	10367(15)	3465(12)	27(6)
H(44)	10336(17)	10666(15)	4223(12)	24(6)
H(45)	9315(18)	9647(16)	4439(12)	29(6)
H(46)	9220(17)	8338(15)	3943(12)	23(6)
H(52)	8270(20)	7490(16)	1608(14)	34(7)
H(53)	7930(20)	7664(16)	459(14)	32(7)

H(54)	9149(18)	7672(14)	-66(13)	24(6)
H(55)	10750(20)	7494(16)	612(14)	35(7)
H(56)	11120(20)	7344(17)	1779(15)	41(8)
H(62)	9910(20)	5355(19)	2907(15)	43(8)
H(63)	10344(19)	4237(18)	3611(14)	40(7)
H(64)	11050(20)	4490(20)	4750(17)	62(10)
H(65)	11410(30)	5840(20)	5151(19)	79(12)
H(66)	10870(20)	6930(20)	4401(15)	52(9)
H(71A)	7458(19)	455(17)	1241(13)	33(7)
H(71B)	6420(20)	721(17)	1269(14)	39(7)
H(72A)	6330(40)	-450(30)	1860(20)	119(18)
H(72B)	6910(30)	-780(20)	1444(19)	75(12)
H(73A)	7620(20)	-840(20)	2740(18)	71(11)
H(73B)	8440(30)	-600(20)	2291(19)	82(12)
H(74A)	7600(30)	520(20)	2983(18)	70(12)
H(74B)	8630(40)	630(30)	2940(20)	127(18)

Scheme 1[a]



[a] Conditions: toluene, 110 °C, 6 h.

Synthesis of **4** and **5**: a mixture of the triorganotin precursor (**1** or **3**, 1 mmol) and 1,5-naphthalenedisulfonic acid (**2**, 2 mmol) were taken up in toluene (60 mL) and heated under reflux for 6 h using a Dean–Stark apparatus to remove the water formed in the reaction by azeotropic distillation. A white solid formed in the reaction was filtered and dried to obtain **4** and **5** in good yields. Crystals suitable for single-crystal X-ray diffraction were obtained by the slow evaporation of a solution of **4** or **5** in a mixture of THF and CH_3OH (1:1) at room temperature. Data for **4** are as follows. Yield: 1.1 g (96%). Mp: 305 °C dec. Anal. Calcd for $C_{38}H_{72}O_{22}S_4Sn_2$ (1246.58): C, 36.61; H, 5.82. Found: C, 36.22; H, 5.51. IR (KBr, cm^{-1}): 3446 [br, $\nu(H_2O)$], 1205 [s, $\nu(SO_3)$ as str], 1163 [s, $\nu(SO_3)$ as str], 1043 [s, $\nu(SO_3)$ ionic], 611 [m, ν(C–S) str]. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.88 (t, J = 7.2 Hz, CH_3), 1.14 (t, J = 8.4 Hz, Sn–CH_2), 1.26–1.35 (m, CH_2), 1.53–1.64 (m, CH_2), 7.44 (t, J = 8.0 Hz, aromatic), 7.95 (d, J = 7.6 Hz, aromatic), 8.85 (d, J = 8.4 Hz, aromatic). ^{119}Sn NMR (150 MHz, DMSO-d_6): δ 8.31 (s), −385.76 (s). Data for **5** are as follows. Yield: 1.0 g (96%). Mp: 170 °C initial dec. Anal. Calcd for $C_{50}H_{46}O_8S_2Sn_2$ (1004.34): C, 55.01; H, 4.30. Found: C, 54.45; H, 3.98. IR (KBr, cm^{-1}): 3445 [br, $\nu(H_2O)$], 1204 [s, $\nu(SO_3)$ as str], 1164 [s, $\nu(SO_3)$ as str], 1042 [s, $\nu(SO_3)$ ionic], 610 [m, ν(C–S) str]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–8.81 (m, naphthyl), 7.37–7.40 (m, phenyl). ^{119}Sn NMR (150 MHz, DMSO-d_6): δ −194 (s).

The structures were solved by direct methods and refined by using full-matrix least squares on F^2 (SHELXS-97). Crystal data for **4**: crystal dimensions 0.2 × 0.2 × 0.2 mm, molecular formula $C_{38}H_{72}O_{22}S_4Sn_2$, M_r = 1246.58, triclinic, space group $P\bar{1}$, a = 9.093(3) Å, b = 11.484(4) Å, c = 14.0584(4) Å, α = 113.35(4)°, β = 94.59(4)°, γ = 100.65(4)°, V = 1305.3(7) Å^3, Z = 1, ρ_{calcd} = 1.586 Mg/m^3, T = 213(2) K, 8257 reflections collected, 3847 independent reflections (R(int) = 0.0460), Mo Kα radiation, λ = 0.710 73 Å, completeness to θ = 24.16°, final R indices ($I > 2\sigma(I)$) R1 = 0.0335 and wR2 = 0.0886, R indices (all data) R1 = 0.0378 and wR2 = 0.0906, GOF = 1.031, largest difference peak and hole 1.307 and −1.240 e Å^{-3}. All the hydrogens of the water molecules were located from the difference map and refined. Crystal data for **5**: crystal dimensions 0.2 × 0.1 × 0.3 mm, molecular formula $C_{50}H_{46}O_8S_2Sn_2$ M_r = 1076.37, monoclinic, space group $P2_1/c$, a = 14.3593(6) Å, b = 15.9365(7) Å, c = 20.5615(9) Å, β = 107.4430-(10)°, V = 4488.9(3) Å^3, Z = 4, ρ_{calcd} = 1.593 Mg/m^3, T = 100(2) K, 27 492 reflections collected, 10 292 independent reflections (R(int) = 0.0220), Mo Kα radiation, λ = 0.710 73 Å, completeness to θ = 27.30°, absorption correction semiempirical, final R indices ($I > 2\sigma(I)$) R1 = 0.0246 and wR2 = 0.0623, R indices (all data) R1 = 0.0280 and wR2 = 0.0640, GOF = 1.023, largest difference peak and hole 1.449 and −0.465 e Å^{-3}. All the hydrogens of the water molecules were located from the difference map and refined.