Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2018

Supplementary Information

Cooperative Metal–Ligand Influence on the Formation of Coordination Polymers, Conducting and Photophysical Properties of Tl(I) β-oxodithioester Complexes†

Chote Lal Yadav[a], Gunjan Rajput[b], Krishna K. Manar[a], Kavita Kumari[a], Michael G. B. Drew[c] and Nanhai Singh*[a]

[a]*Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi-221005, India.*
[b]*Department of Chemistry, Ram Chandra Uniyal Government PG College, Uttarkashi-249193, India.*
[c]*Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK .*

†Part of the work presented at ISACS: Challenges in Inorganic Chemistry, April 10-13, 2017, Manchester, UK.

E-mail: nsinghbhu@gmail.com, nsingh@bhu.ac.in

Contents

Table S5: Selected bond lengths (Å) and angles (°) for complexes **7a**

Table S6: Intermolecular interactions of note in **3**, **4** and **6**, distances (Å) angles (°)

S1: Characterization data for ligands L1–L8

[**L1**] Yield: (0.174 g, 84%). Anal. Calcd for: $C_8H_8O_2S_2$ (200.): C 46.12, H 7.74%. Found: C 46.02, H 7.79%. IR (KBr, cm^{-1}): ν = 1085 ($\nu_{C–OH}$), 1613 ($\nu_{C=C}$), 1226 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.55 (s, 3H, –SCH_3), 6.83 (s, 1H, –CH=C–), 6.46–7.49 (m, 3H, –C_4H_3O), 14.62 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.20 (–SCH_3), 106.56 (–CH=C), 112.79, 115.32, 145.87, 148.76 (–C_4H_3O), 159.37 (–C(OH)–), 216.80 (–C=S) ppm.

[**L2**] Yield: (0.186 g, 86%). Anal. Calcd for: $C_8H_8OS_3$ (216.33): C 44.41, H 3.73%. Found: C 44.35, H 3.78%. IR (KBr, cm^{-1}): ν = 1061 ($\nu_{C–OH}$), 1576 ($\nu_{C=C}$), 1232 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.55 (s, 3H, –SCH_3), 6.77 (s, 1H, –CH=C–), 7.02–7.64 (m, 3H, –C_4H_3S), 14.97 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.13 (–SCH_3), 107.17 (–CH=C–), 128.56, 129.42, 135.15, 138.55 (–C_4H_3S), 164.23 (–C(OH)–), 215.92 (–C=S) ppm.

[**L3**] Yield: (0.147 g, 70%). Anal. Calcd for: $C_9H_9NOS_2$ (211.30): C 51.16, H 4.29, N 6.63%. Found: C 51.05, H 4.36, N 6.70%. IR (KBr, cm^{-1}): ν = 1124 ($\nu_{C–OH}$), 1591 ($\nu_{C=C}$), 1227 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.55 (s, 3H, –SCH_3), 6.82 (s, 1H, =CH–C(S)–), 7.28–8.99 (m, 4H, C_5H_4N), 14.89 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.39 (–SCH_3), 107.98 (–CH=C–), 123.64, 130.31, 134.00, 147.86, 152.19 (–C_5H_4N), 166.17 (–C(OH)–), 218.39 (–C=S) ppm.

[**L4**] Yield: (0.152 g, 72%). Anal. Calcd for: $C_9H_9NOS_2$ (211.30): C 51.16, H 4.29, N 6.63%. Found: C 51.08, H 4.38, N 6.72%. IR (KBr, cm^{-1}): ν = 1060 ($\nu_{C–OH}$), 1587 ($\nu_{C=C}$), 1217 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.60 (s, 3H, –SCH_3), 6.85 (s, 1H, –CH=C–), 7.61–8.74 (m, 4H, –C_5H_4N), 14.78 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.56 (–SCH_3), 108.26 (–CH=C–), 120.04, 141.95, 150.63 (–C_5H_4N), 165.30 (–C(OH)–), 219.27 (–C=S) ppm.

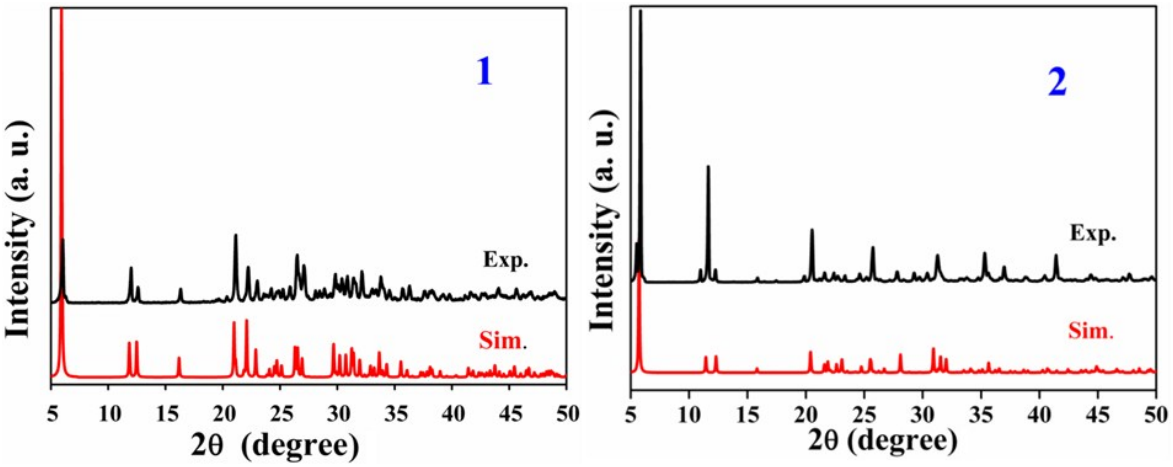
[**L5**] Yield: (0.204 g, 66%). Anal. Calcd for: $C_{18}H_{14}OS_2$ (310.43): C 69.64, H 4.55%. Found: C 69.57, H 4.68%. IR (KBr, cm^{-1}): ν = 1140 ($\nu_{C–OH}$), 1580 ($\nu_{C=C}$), 1227 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.70 (s, 3H, $–SCH_3$), 6.87 (s, 1H, –CH=C–), 7.25–8.52 (m, 9H, $–C_{14}H_9$), 15.37 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.11 ($–SCH_3$), 115.17 (–CH=C–). 124.72, 125.31, 126.74, 127.26, 128.47, 129.23, 131.00, 134.06 ($–C_{14}H_9$), 170.18 (–C(OH)–), 218.69 (–C=S) ppm.

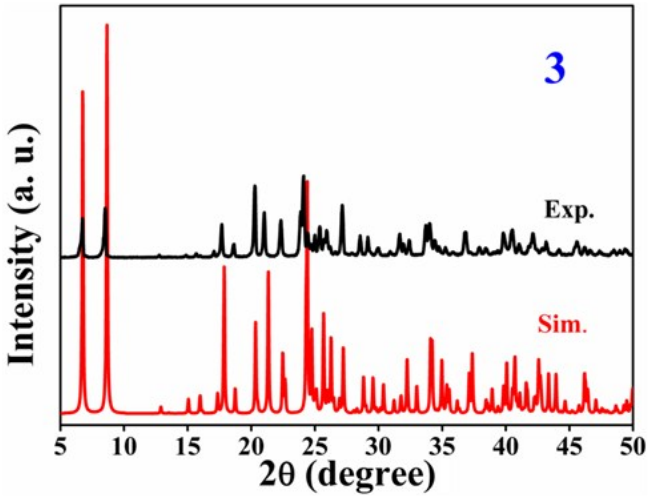
[**L6**] Yield: (0.200 g, 88%). Anal. Calcd for: $C_{10}H_9FOS_2$ (228.31): C 52.61, H 3.97%. Found: C 52.42, H 4.10%. IR (KBr, cm^{-1}): ν = 1165 ($\nu_{C–OH}$), 1601 ($\nu_{C=C}$), 1229 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.59 (s, 3H, $–SCH_3$), 6.83 (s, 1H, –CH=C–), 7.04–7.83 (m, 4H, $–C_6H_4F$), 15.03 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.20 ($–SCH_3$), 107.61 (–CH=C–), 122.95, 129.63, 134.58, 136.39, ($–C_6H_4F$), 167.09 (–C(OH)–), 216.62 (–C=S) ppm.

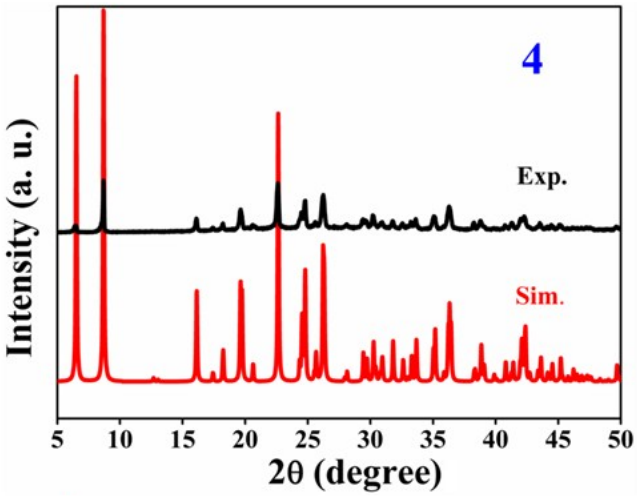
[**L7**] Yield: (0.208 g, 85%). Anal. Calcd for: $C_{10}H_9ClOS_2$ (244.76): C 49.07, H 3.71%. Found: C 48.95, H 3.85%. IR (KBr, cm^{-1}): ν = 1121 ($\nu_{C–OH}$), 1582 ($\nu_{C=C}$), 1234 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.64 (s, 3H, $–SCH_3$), 6.88 (s, 1H, –CH=C–), 7.39–7.80 (m, 4H, $–C_6H_4Cl$), 15.03 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.13 ($–SCH_3$), 107.53 (–CH=C–), 127.84, 128.96, 132.57, 137.88, ($–C_6H_4Cl$), 167.58 (–C(OH)–), 217.44 (–C=S) ppm.

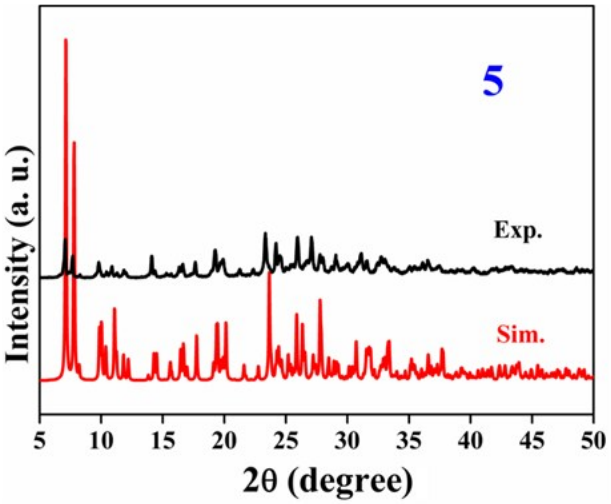
[**L8**] Yield: (0.266 g, 92%). Anal. Calcd for: $C_{10}H_9BrOS_2$ (289.21): C 41.53, H 3.14%. Found: C 41.45, H 3.24%. IR (KBr, cm^{-1}): ν = 1117 ($\nu_{C–OH}$), 1584 ($\nu_{C=C}$), 1236 ($\nu_{C=S}$). ^1H NMR (500.15 MHz, $CDCl_3$): δ 2.66 (s, 3H, $–SCH_3$), 6.90 (s, 1H, –CH=C–), 7.57–7.83 (m, 4H, $–C_6H_4Br$), 15.04 (s, 1H, –C(OH)–) ppm. $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$): δ 17.33 ($–SCH_3$), 107.69 (–CH=C–), 126.57, 128.17, 129.93, 132.13, ($–C_6H_4Br$), 167.84 (–C(OH)–), 217.73 (–C=S) ppm.

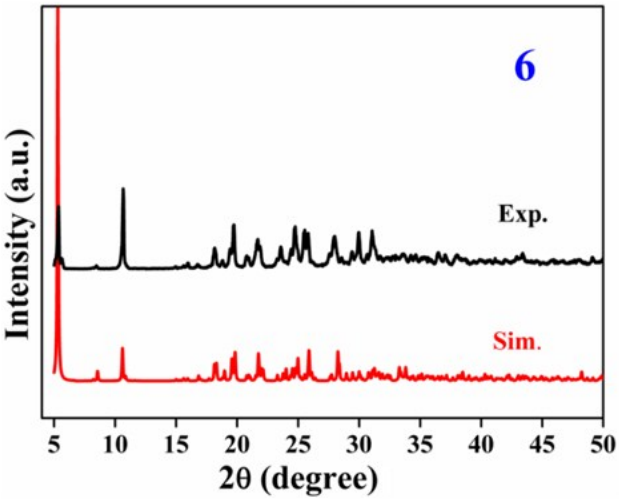
Figure S1 Simulated (in red, generated from single crystal data) and experimental (in black) PXRD patterns of complexes of **1–8**

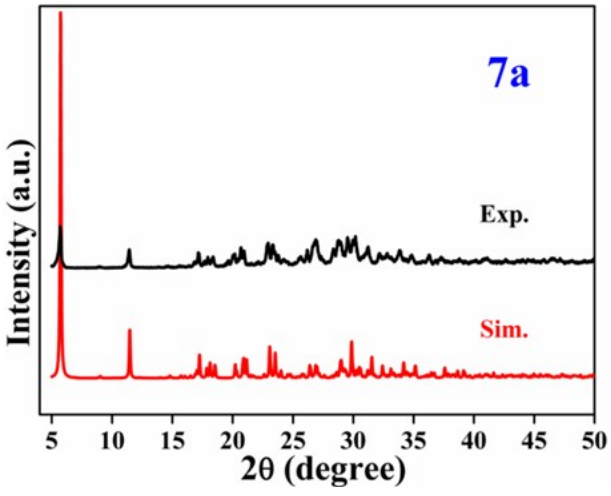


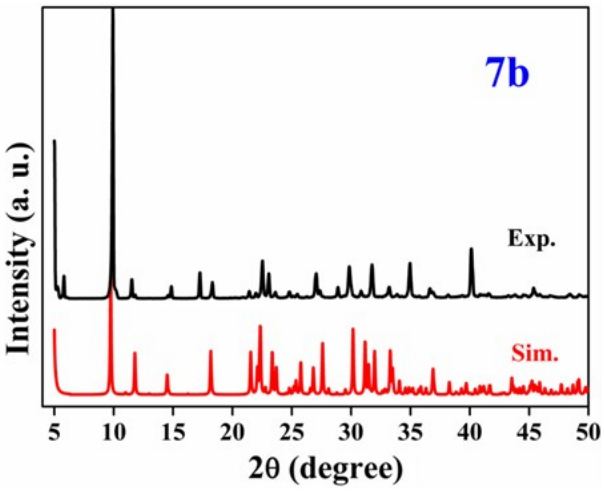

3
Exp.
Sim.
Intensity (a. u.)
2θ (degree)


4
Exp.
Sim.
Intensity (a. u.)
2θ (degree)


5
Exp.
Sim.
Intensity (a. u.)
2θ (degree)


6
Exp.
Sim.
Intensity (a.u.)
2θ (degree)


7a
Exp.
Sim.
Intensity (a.u.)
2θ (degree)


7b
Exp.
Sim.
Intensity (a. u.)
2θ (degree)

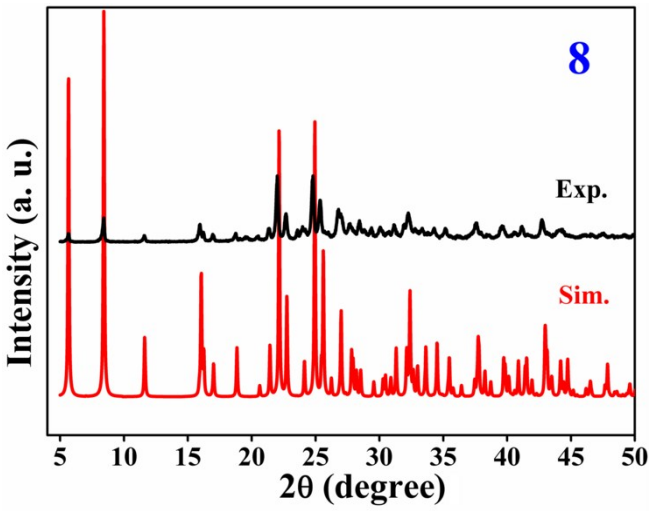


Figure S2 (a) UV-Vis. spectra of complexes as solid in nujol mull; (b) and (c) their emission spectra in the solid phase

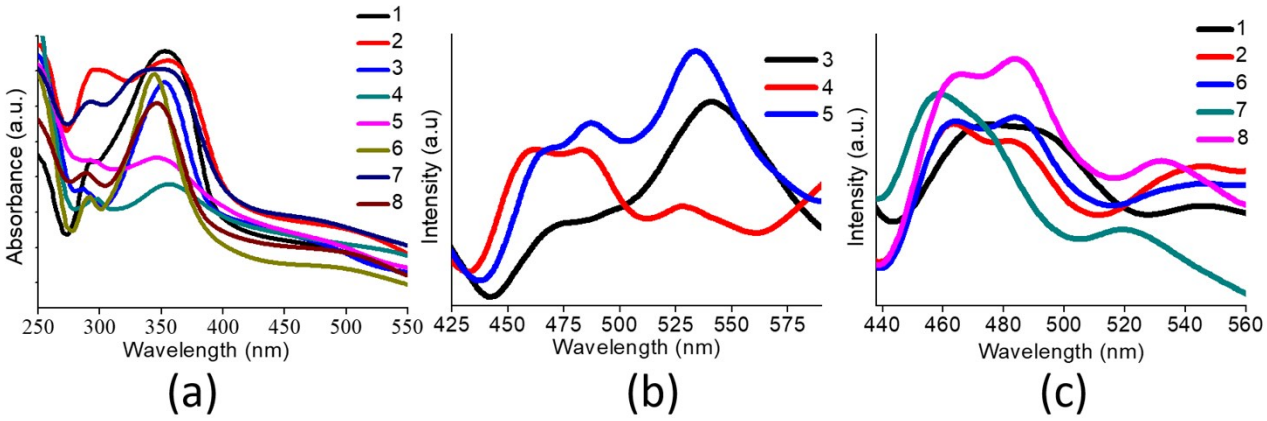


Figure S3 Non-covalent interactions in **3**, **4**, **6** and **7b**

Figure S3.1 C–H···N, C–H···O and H···H interactions in **3** (left) and C–H···N, C–H···π interactions in **4** (right)

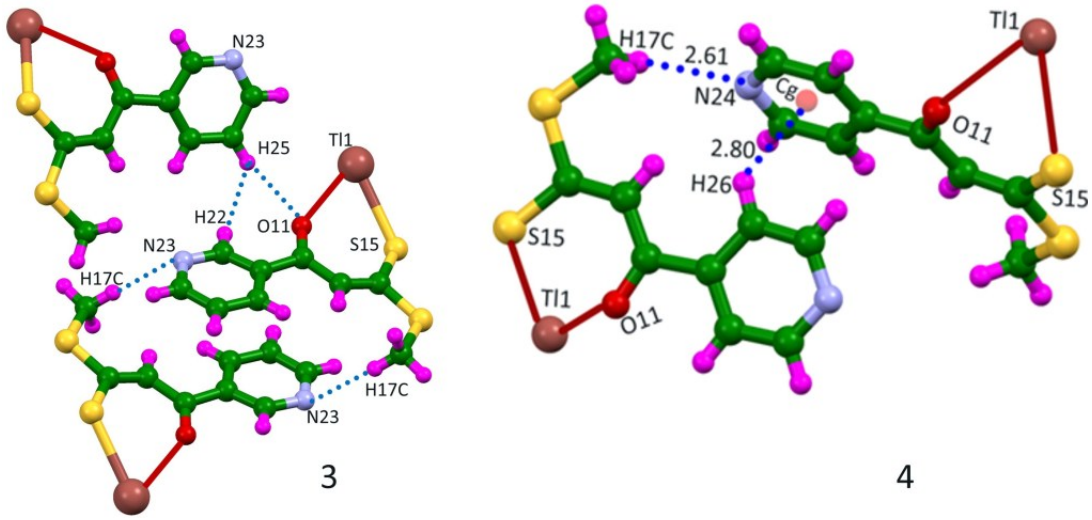


Figure S3.2 Supramolecular structures of **6** sustained by C–H···F and H···H interactions (C–H···O interactions omitted for clarity) and **7b** by C–H···Cl (hydrogen atoms omitted for clarity)

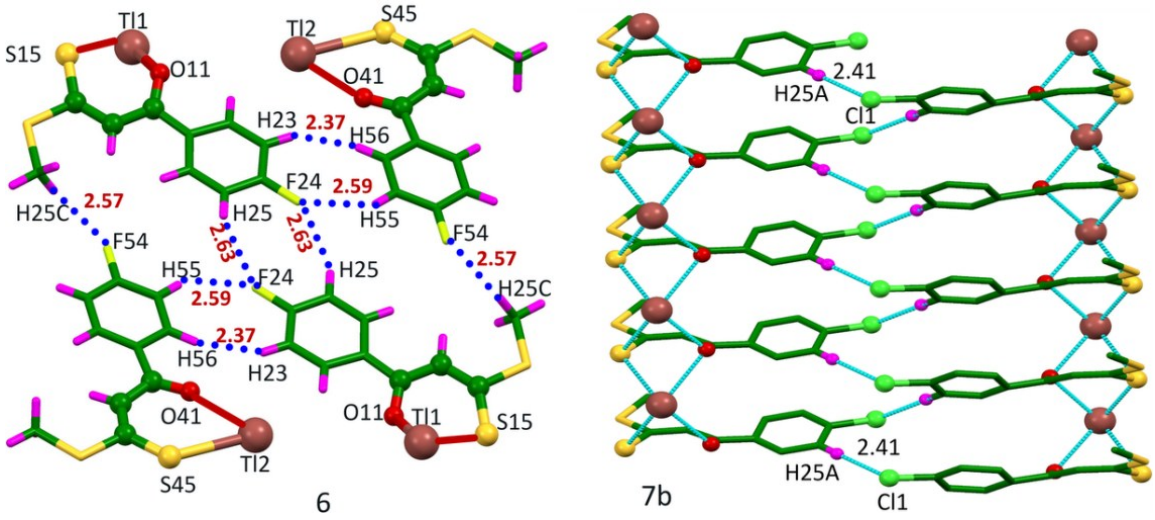


Figure S4 Temperature dependent pressed pellet conductivity plots for complexes **1–8**

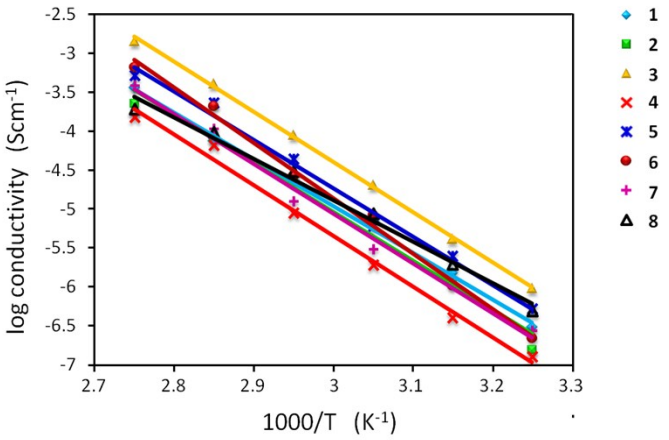


Figure S5 Solid state CD spectra of complexes **1** and **2** recorded at room temperature by dispersing powder samples in KBr pellets

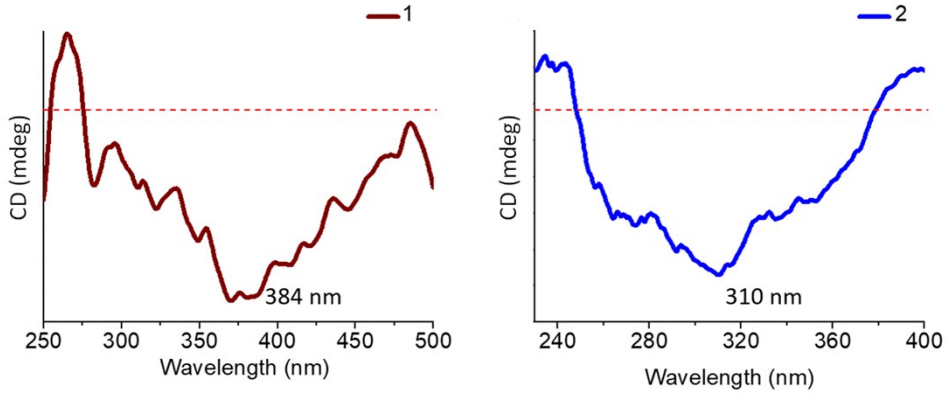


Table S1. Crystallographic parameters for the ligand L5 and complexes **1**–**8**

Compound	**L5**	**1**	**2**	**3**	**4**
Chemical formula	$C_{18}H_{14}O\ S_2$	$C_8H_7O_2S_2Tl$	$C_8H_7OS_3Tl$	$C_9H_8NOS_2Tl$	$C_9H_8NOS_2Tl$
Formula weight	310.41	403.63	419.69	414.65	414.65
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*-1	$P2_1$	$P2_12_12_1$	*P*ccn	*I*ba2
a(Å)	8.6083(7)	4.2030(10)	4.1521(4)	11.0854(5)	10.9680(7)
b (Å)	9.1906(8)	8.045(2)	8.1183(7)	26.1784(12)	27.114(2)
c (Å)	10.2695(8)	14.929(5)	30.921(4)	7.1879(3)	7.1755(5)
α (°)	78.227(7)	90	90	90	90
β (°)	68.521(7)	91.16(2)	90	90	90
γ (°)	78.296(7)	90	90	90	90
V (Å³)	732.79(10)	504.7(2)	1042.30(19)	2085.91(16)	2133.9(3)
Z	2	2	4	8	8
ρ_{calc}(g cm^{-3})	1.407	2.656	2.674	2.641	2.581
T (K)	150(2)	100(2)	150(2)	100(2)	295(2)
μ (Mo Kα) (mm^{-1})	0.358	16.376	16.051	15.849	15.493
F(000)	324	368	768	1520	1520
Reflections collected	5170	9305	6247	28722	14954
Independent reflections	4074	2354	3012	2402	2655
Reflections with I > 2σ(I)	3460	2270	2559	1977	2197
Final indices[I>2σ(I)]R_1[a], wR_2[b]	0.0404, 0.0993	0.0418, 0.1453	0.0692, 0.1625	0.0233, 0.0506	0.0352, 0.0758
$R_{1[a]}$,$wR_{2[b]}$[all data]	0.0503, 0.1049	0.0431, 0.1471	0.0813, 0.1703	0.0365, 0.0545	0.0479, 0.0806
GOF [c]	1.044	1.113	1.054	0.991	1.088
Residual electron Density, e/Å^{-3}	0.370, -0.321	1.983, -2.064	4.494, -3.662	0.782, -1.034	0.651, -1.848
Flack Parameter	-	0.12(3)	-0.01(2)	-	-

Compound	**5**	**6**	**7a**	**7b**	**8**
Chemical formula	$C_{36}H_{26}O_2S_4Tl_2$	$C_{20}H_{16}F_2O_2S_4Tl_2$	$C_{30}H_{24}Cl_3O_3S_6Tl_3$	$C_{10}H_8ClOS_2Tl$	$C_{10}H_8BrOS_2Tl$
Formula weight	1027.55	863.31	1344.31	448.10	492.56
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*-1	$P2_1$/c	$P2_1$/c	*P*na2_1	*I*ba2
a(Å)	11.1320(7)	17.9716(9)	16.4850(11)	8.2435(6)	31.252(5)
b (Å)	11.5849(7)	6.0317(2)	18.2914(10)	36.287(4)	11.1332(14)
c (Å)	12.7090(8)	22.2375(11)	12.6565(8)	4.0103(4)	6.9522(7)
α (°)	82.345(5)	90	90	90	90
β (°)	78.454(5)	111.937(6)	110.753(8)	90	90
γ (°)	79.481(5)	90	90	90	90
V (Å³)	1570.87(17)	2235.99(17)	3568.7(4)	1199.61(19)	2418.9(5)
Z	2	4	4	4	8
ρ_{calc}(g cm^{-3})	2.172	2.565	2.502	2.481	2.705

T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
μ (Mo Kα) (mm^{-1})	10.545	14.801	14.121	14.003	16.972
F(000)	968	1584	2472	824	1792
Reflections collected	11126	14165	13164	4221	8051
Independent reflections	8776	6452	7863	1959	2962
Reflections with I > 2σ(I)	6677	4715	5122	1538	1805
Final indices[I>2σ(I)]R[a], wR_2[b]	0.0536, 0.1091	0.0768, 0.2164	0.0721, 0.1810	0.0634, 0.1443	0.0690, 0.1265
$R_{1[a]}$,$wR_{2[b]}$ [all data]	0.0775, 0.1197	0.1077, 0.2463	0.1160, 0.2103	0.0820, 0.1601	0.1257, 0.1486
GOF [c]	0.988	1.064	0.969	1.093	0.953
Residual electron Density, e/Å^{-3}	2.839, -3.254	4.491, -4.727	3.776, -3.232	2.4093, -1.564	3.218, -2.223
Flack Parameter	-	-	-	-	-

[a]$R_1 = \Sigma \left\| F_o \right| - \left| F_c \right\| / \Sigma \left| F_o \right|$, [b]$wR_2 = \{[\Sigma w (F_o^2 - F_c^2)/ \Sigma w (F_o^2)^2]\}^{/2}$,[c]GOF= S= $\{ \Sigma [w(F_o^2-F_c^2)^2]/(n-p)\}^{/2}$, where n is the number of reflections, and p is the number of the refined parameters.

Table S2. Selected Bond Lengths (Å) and Angles (°) for Complexes **1**–**4, 7b** and **8**

	1	**2**	**3**	**4**	**7**b	**8**
Tl1–O11	2.795(12)	2.812(13)	2.724(3)	2.867(8)	3.00(3)	2.869(16)
Tl1–S15	3.109(4)	3.132(5)	2.893(1)	3.020(3)	3.108(11)	2.989(6)
Tl1–O11$1	3.271(17)	3.157(16)			2.87(3)	3.137(17)
Tl1–S15$1	3.191(5)	3.148(5)	3.024(1)	3.118(2)	3.156(11)	3.053(6)
Tl1–S15$3	3.273(4)	3.256(5)	3.187(1)	3.090(3)	3.306(10)	3.115(6)
Tl1–S15$2	3.366(4)	3.316(5)			3.261(10)	
Tl1–S16$3	3.411(5)	3.327(6)	3.590(1)	3.813(3)	3.485(8)	
Tl1···Tl1$1	4.203(10)	4.152(1)	4.974(1)		4.010(4)	4.605(1)
Tl1···Tl1$2	4.548(10)	4.575(1)	4.974(1)	4.803(1)	4.636(7)	4.605(1)
Tl1···Tl1$5					4.636(7)	
Tl1···Tl1$3				4.803(1)		
O11–Tl1–S15	65.2(3)	64.4(3)	67.55(7)	60.99(16)	62.5(4)	61.9(4)
O11–Tl1–O11$1	87.3(4)	87.9(4)			86.1(4)	72.9(4)
O11–Tl1–S15$1	114.9(4)	115.3(3)	88.85(7)	117.44(16)	115.7(5)	121.6(3)
O11–Tl1–S15$3	96.0(4)	94.2(3)	128.95(7)	117.84(18)	153.0(3)	117.5(4)
O11–Tl1–S15$2	152.3(3)	152.4(3)			92.5(6)	
O11–Tl1–S16$3	123.1(3)	121.2(3)	174.51(7)		150.8(5)	
S15–Tl1–O11$1	119(3)	118.8(3)			113.6(4)	
S15–Tl–S15$1	83.69(13)	82.77(10)	88.21(2)	61.46(6)	79.61(11)	88.91(14)
S15–Tl1–S15$3	86.90(5)	86.69(5)	61.43(4)	89.04(67)	139.48(7)	61.21(19)

S15–Tl1–S15$2	140.09(7)	139.83(7)			89.6(4)	
S15–Tl1–S16$3	68.14(11)	67.27(12)	110.24(3)		90.30(16)	
O11$1–Tl1–S15$1	59.2(3)	60.5(3)			63.2(5)	72.9(4)
O11$1–Tl1–S15$3	152.5(4)	152.2(3)			116.5(7)	117.5(4)
O11$1–Tl1–S15$2	86.0(4)	87.0(2)			152.5(3)	
O11$1–Tl1–S16$3	145.0(2)	145.9(3)			150.8(5)	
S15$1–Tl1–S15$3	139.79(6)	139.83(3)	87.83(3)	83.16(5)	87.9(3)	
S15$1–Tl1–S15$2	84.04(5)	85.39(5)			139.38(7)	80.64(11)
S15$1–Tl1–S16$3	89.92(10)	89.09(12)	86.03(3)		65.26(15)	
S15$3–Tl1–S15$2	78.55(9)	78.35(9)			75.27(10)	
S15$3–Tl1–S16$3	50.54(11)	51.31(11)	48.92(3)		49.84(14)	
S15$2–Tl1–S16$3	74.02(11)	74.69(12)			75.9(2)	
Tl1···H17$4	3.30	3.24	3.43	3.44	3.41	3.47
Tl1···H17$4–C17$4	124	130	135	126	118	124
Tl1···H24$5			3.34			
Tl1···H24$5–C24$5			137			
Tl1···H25$5				3.39		
Tl1···H25$5–C25$5				124		

Symmetry elements

In **1** $1 = x-1,y,z $2 -x, y+1/2,-z $3 -x+1, y+1/2, -z $4 -1+x,1+y,z

In **2** $1 = x-1,y,z $2 1-x, y-1/2,-3/2-z $3 -x, y-1/2, -3/2-z $4 -1+x, -1+y,z

In **3** $1 = ½-x, y, ½+z $2 = ½-x, -1+y, ½+z $3 = ½-x, ½-y, z $4 ½-x, y, z-1/2 $5 ½+x, 1-y,3/2-z

In **4** $1 = 1-x, y, z+1/2 $2 = 1-x, y, z-1/2 $3 = 1-x, 1-y, z $4 = 1-x y, z-1/2 $5 x-1/2, 3/2-y, z

In **7b**$1= x,y,1+z $2 = x-1/2, 3/2-y, z $3 x-1/2, 3/2-y, 1+z $4 -1+x,y,1+z $5 x+1/2, 3/2-y, 1+z

In **8** $1 = x 1-y, z-1/2 $2 x, 1-y, z+1/2 $3 1-x, 1-y, z $4 x,1-y,z+1/2

Table S3. Selected bond lengths (Å) and angles (°) for complex **5**

Tl1–O11	2.651(5)	Tl2–O41	2.572(5)
Tl1–S15	2.943(2)	Tl2–O11	2.904(6)
Tl1–S45	3.086(2)	Tl2–S45	3.041(2)

Tl1–O41	2.848(5)	Tl2–S15	3.061(2)
Tl1–S45$1	3.511(2)	Tl2–S16$2	3.557(2)
O11–Tl1–O41	62.29(14)	O41–Tl2–O11	62.35(11)
O11–Tl1–S15	68.15(12)	O41–Tl2–S45	67.65(13)
O41–Tl1–S15	96.69(11)	O11–Tl2–S45	98.21(11)
O11–Tl1–S45	102.89(12)	O41–Tl2–S15	100.02(12)
O41–Tl1–S45	63.95(12)	O11–Tl2–S15	63.55(11)
S15–Tl1–S45	68.00(5)	S45–Tl2–S15	67.12(4)
O11–Tl1–S45$1	124.18(11)	O41–Tl2–S16$2	102.92(13)
O41–Tl1–S45$1	161.45(12)	O11–Tl2–S16$2	119.06(11)
S15–Tl1–S45$1	72.88(5)	S45–Tl2–S16$2	132.39(5)
S45–Tl1–S45$1	97.62(4)	S15–Tl2–S16$2	154.65(4)
Tl1···Tl1$1	4.356(1)		
Tl1···Tl2	3.724(1)		
Tl2···Tl2$2	4.348(1)		
Tl1···H47$1	3.23	Tl1···H47$1–C47$1	143
Tl1···H31$3	3.34	Tl1···H31$3–C31$3	138
Tl1···H21	3.50	Tl1···H21–C21	158
Tl1···H51	3.30	Tl1···H51–C51	136
Tl2···H32$1	3.23	Tl2···H32$1–C32$1	122

Symmetry elements $1 = 2-x, 1-y, 1-z $2 1-x, 1-y, 1-z $3 1-x,-y,-z

Table S4. Selected bond lengths (Å) and angles (°) for complex **6**

Tl1–O11	2.596(10)	Tl2–O11	2.732(9)
Tl1–S15	3.059(4)	Tl2–O41	2.840(12)
Tl1–S45$1	3.266(4)	Tl2–S45	2.998(3)

Tl1–S15$2	3.300(4)	Tl2–S15	3.562(3)
Tl1–S15$3	3.436(3)	Tl2–S45$1	3.209(4)
Tl1–S16$2	3.567(4)	Tl2–S46$5	3.407(3)
Tl1–S46$1	3.717(4)		
O11–Tl1–S15	64.1(2)	O11–Tl2–O41	77.4(3)
O11–Tl1–S45$1	86.1(2)	O11–Tl2–S45	86.2(2)
S15–Tl1–S45$1	92.8(1)	O41–Tl2–S45	66.1(2)
O11–Tl1–S15$2	133.1(2)	O11–Tl2–S45$1	85.0(2)
S15–Tl1–S15$2	94.60(9)	O41–Tl2–S45$1	125.3(2)
S45$1–Tl1–S15$2	138.79(10)	S45–Tl2–S45$1	61.30(12)
O11–Tl1–S15$3	82.8(2)	O11–Tl2–S46$6	156.7(2)
S15–Tl1–S15$3	136.39(13)	O41–Tl2–S46$6	80.0(2)
S45–Tl1–S15$3	113.29(8)	S45–Tl2–S46$6	79.40(9)
S15$2–Tl1–S15$3	87.92(10)	S45$1–Tl2–S46$6	103.60(9)
O11–Tl1–S16$2	157.1(2)	O11–Tl2–S15	55.6(2)
S15–Tl1–S16$2	93.55(9)	O41–Tl2–S15	122.3(2)
S45$1–Tl1–S16$2	90.42(9)	S45–Tl2–S15	131.89(10)
S15$2–Tl1–S16$2	48.72(9)	S45$1–Tl2–S15	85.06(9)
S15$3–Tl1–S16$2	119.17(9)	S46$6–Tl2–S15	145.53(8)
O11–Tl1–S46$1	99.4(2)		
S15–Tl1–S46$1	59.58(2)		
S45$1–Tl1–S46$1	47.45(8)		
S15$2–Tl1–S46$1	104.34(9)		
S15$3–Tl1–S46$1	159.89(8)		
S16$2–Tl1–S46$1	62.55(7)		
Tl1···Tl1$5	4.577(1)		
Tl1···Tl2$4	4.098(1)		
Tl1···Tl1$2	4.572(1)		
Tl2···Tl2$6	4.237(1)		
Tl1···H47$7	3.21	Tl1···H47$7–C47$7	132
Tl2···H22$8	3.21	Tl2···H22$8–C22$8	139

Symmetry elements $1 1-x, 1-y, z $2 1-x, y-1/2, -z-1/2 $3 x, -1+y,z

$4 1-x y+1/2, -3/2-z $5 x, 1+y, z $6 1-x, 2-y, -z

Table S5. Selected bond lengths (Å) and angles (°) for complex **7a**

Tl1–O31	2.794(12)	Tl2–O11	2.629(12)	Tl3–O31	3.008(11)

Tl1–O51	2.760(14)	Tl2–S15	3.137(4)	Tl3–O11$2	3.031(12)
Tl1–S35	3.196(4)	Tl2–S35	3.291(4)	Tl3–S15	3.139(4)
Tl1–S55	3.241(4)	Tl2–O51$1	2.845(16)	Tl3–S55$3	3.097(4)
Tl1–S35$1	3.345(4)	Tl2–S55$4	3.371(4)	Tl3–S15$2	3.297(4)
Tl1–S15$2	3.424(4)	Tl2–S55$1	3.283(4)	Tl3–S35	3.445(4)
Tl1–S36$1	3.534(5)			Tl3–S16	3.572(4)
Tl1–S16$2	3.618(5)			Tl3–S56$3	3.581(5)
O51–Tl1–O31	87.5(4)	O11–Tl2–O51$1	77.3(4)	O31–Tl3–O11$2	118.4(3)
O51–Tl1–S35	88.5(3)	O11–Tl2–S15	63.9(2)	O31–Tl3–S55$3	114.0(2)
O31–Tl1–S35	62.1(2)	O51$1–Tl2–S15	87.2(3)	O11$2–Tl3–S55$3	62.6(2)
O51–Tl1–S55	61.0(3)	O11–Tl2–S55$1	82.7(3)	O31–Tl3–S15	124.6(2)
O31–Tl1–S55	89.9(3)	O51$1–Tl2–S55$1	59.7(3)	O11$2–Tl3–S15	116.4(2)
S35–Tl1–S55	140.21(13)	S15–Tl2–S55$1	137.91(14)	S55$3–Tl3–S15	83.78(10)
O51–Tl1–S35$1	63.5(3)	O11–Tl2–S35	124.4(3)	O31–Tl3–S15$2	65.0(2)
O31–Tl1–S35$1	130.9(2)	O51$1–Tl2–S35	63.5(3)	O11$2–Tl3–S15$2	58.1(2)
S35–Tl1–S35$1	77.55(10)	S15–Tl2–S35	75.79(10)	S55$3–Tl3–S15$2	103.70(10)
S55–Tl1–S35$1	106.49(10)	S55$1–Tl2–S35	106.79(10)	S15–Tl3–S15$2	164.70(19)
O51–Tl1–S15$2	130.1(3)	O11–Tl2–S55$4	62.7(3)	O31–Tl3–S35	57.1(2)
O31–Tl1–S15$2	65.3(2)	O51$1–Tl2–S55$4	128.9(3)	O11$2–Tl3–S35	161.3(2)
S35–Tl1–S15$2	110.84(11)	S15–Tl2–S55$4	101.15(10)	S55$3–Tl3–S35	136.01(13)
S55–Tl1–S15$2	77.27(9)	S55$1–Tl2–S55$4	83.77(11)	S15–Tl3–S35	73.56(10)
S35$1–Tl1–S15$2	162.55(13)	S35–Tl2–S55$4	167.43(13)	S15$2–Tl3–S35	107.91(10)
O51–Tl1–S36$1	101.4(3)			O31–Tl3–S16	168.8(2)
O31–Tl1–S36$1	166.4(2)			O11$2–Tl3–S16	69.8(2)
S35–Tl1–S36$1	107.46(11)			S55$3–Tl3–S16	76.26(11)
S55–Tl1–S36$1	103.40(11)			S15–Tl3–S16	49.65(12)
S35$1–Tl1–	48.23(11)			S15$2–Tl3–S16	118.53(11)

S36$1					
S15$2–Tl1–S36$1	114.42(12)			S35–Tl3–S16	112.57(9)
O51–Tl1–S16$2	130.6(3)			O31–Tl3–S56$3	66.2(2)
O31–Tl1–S16$2	112.7(2)			O11$2–Tl3–S56$3	96.1(2)
S35–Tl1–S16$2	140.96(10)			S55$3–Tl3–S56$3	49.48(12)
S55–Tl1–S16$2	73.92(11)			S15–Tl3–S56$3	100.21(12)
S35$1–Tl1–S16$2	116.30(11)			S15$2–Tl3–S56$3	94.72(11)
S15$2–Tl1–S16$2	47.56(11)			S35–Tl3–S56$3	97.63(11)
S36$1–Tl1–S16$2	69.22(10)			S16–Tl3–S56$3	122.37(9)
Tl2···Tl3$3	4.037(1)				
Tl1···Tl3	3.767(1)				
Tl1···Tl2$1	3.891(1)				
Tl1···Tl3$2	4.886(1)				
Tl2···H23$5	3.25	Tl2···H23$5–C23$5	148		

Symmetry Elements

$1 -x, -y, 1-z $2 x, ½-y, z-1/2 $3 x, 1/2-y, z+1/2 $4 x,y,1+z $5 -x,-y,2-z

Table S6. Non-classical hydrogen bonding interactions in **3**, **4, 6** and **7b (**distances (**Å**) angles (°)).

In **3**

Donor (D)···Acceptor (A)	H···A	D···A	D–H···A	Symmetry Element
C17–H17C···N23	2.65	3.62	170	1-x, 1-y, -z
C25–H25···O11	2.61	3.54	167	x-1/2, 1-y, 3/2-z
C22–H22···H25	2.33	2.98	125	x+1/2, 1-y, 3/2-z

In **4**

Donor (D)···Acceptor (A)	H···A	D···A	D–H···A	Symmetry Element
C17–H17C···N24	2.61	3.49	149	3/2-x, 3/2-y, z+1/2
C26–H26···CG1	2.80		124, 83*	3/2-x, 3/2-y, z+1/2

* C-H···CG angle between H···CG and aromatic ring

CG1 is ring C21–C26 inclusive

In **6**

Donor (D)···Acceptor (A)	H···A	D···A	D–H···A	Symmetry Element
C25–H25C···F24	2.63	3.22	122	2-x, -y, -z
C25–H25···F54	2.57	3.44	151	2-x, 1-y, -z
C55–H55···F24	2.59	3.16	119	x, 1+y, z

In **7b**

Donor (D)···Acceptor (A)	H···A	D···A	D–H···A	Symmetry Element
C25A–H25C···Cl1	2.41	3.33	170	1-x, 2-y, ½+z