ELECTRONIC SUPPLIMENTARY INFORMATION (ESI)

Influence of ligand environments on the structures and luminescent properties of homoleptic cadmium (II) pyridyl functionalized dithiocarbamates

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Table S1. Selected bond lengths (Å) and angles (°) for complexes **1** and **2.**

Bond Distances	**1**	**2**
Cd(1)—S(11)	2.659(1)	2.680(1)
Cd(1)—S(13)	2.652(1)	2.664(1)
Cd(1)—S(41)	2.665(1)	2.663(1)
Cd(1)—S(43)	2.687(1)	2.665(1)
Cd(1)—N(34) $1	2.539(3)	2.486(3)
Cd(1)—N(64) $2	2.500(3)	2.486(3)
S(11)—C(12)	1.723(3)	1.729(3)
S(13)—C(12)	1.708(3)	1.724(3)
S(41)—C(42)	1.711(3)	1.727(3)
S(43)—C(42)	1.727(3)	1.711(3)
N(14)—C(12)	1.346(4)	1.340(4)
N(44)—C(42)	1.346(4)	1.337(4)
Bond Angles		
S(11)—Cd(1)—S(13)	68.06(3)	67.81(3)
S(41)—Cd(1)—S(43)	67.32(3)	67.95(3)
S(43)—Cd(1)—N(34)$1	92.11(7)	87.14(6)
S(11)—Cd(1)—S(41)	176.55(3)	176.58(2)
S(13)—Cd(1)—S(41)	108.79(3)	108.80(3)
S(11)—Cd(1)—S(43)	115.78(3)	115.44(3)
S(13)—Cd(1)—S(43)	175.79(3)	176.65(3)
S(13)—Cd(1)—N(64)$2	92.38(7)	85.15(7)
S(43)—Cd(1)—N(64)$2	89.44(7)	93.77(7)
S(11)—Cd(1)—N(34)$1	93.31(8)	88.83(7)
S(41)—Cd(1)—N(34)$1	84.96(8)	90.92(7)
N(36)$1—Cd(1)—N(64)$2	176.01(11)	176.96(9)
S(41)—Cd(1)—N(64)$2	92.25(7)	86.74(7)
S(11)—Cd(1)—N(64)$2	89.33(7)	93.39(7)
S(13)—Cd(1)—N(34)$1	85.83(8)	93.78(7)

Symmetry elements

In **1** $1 1-x, 1/2+y, 1.5-z, $2 -x, -1/2+y, 1.5-z

In **2** $1 1-x -1/2+y, 1.5-z $2 2-x, 1/2+y, 1.5-z

Table S2. Selected bond lengths (Å) and angles (°) for complexes**3** and **4.**

Bond Distances	**3**	**4**
Cd(1)—S(11)	2.625(1)	2.614(1)
Cd(1)—S(13)	2.677(1)	2.694(1)
Cd(1)—N(34)$1	2.480(3)	2.502(3)
S(11)—C(12)	1.718(3)	1.719(3)
S(13)—C(12)	1.713(3)	1.717(3)
N(14)—C(12)	1.342(4)	1.341(4)
Bond Angles		
S(11)—Cd(1)—S(13)	68.19(3)	67.99(3)
S(11)—Cd(1)—N(34)$1	89.32(7)	88.15(9)
S(13)—Cd(1)—N(34)$1	93.40(7)	92.08(8)

$1 Symmetry element in **3** 1/2+x, -y-1/2, -z
In **4** 1/2-x, 2-y, -1/2+z

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

Cd (1)-S(11)	2.570(1)	S(11)- Cd(1)-S(13)	68.58(5)
Cd (1)-S(13)	2.690(1)	S(41)- Cd(1)-S(43)	69.05(5)
Cd (1)-S(41)	2.635(1)	N(56)$1- Cd(1)-S(11)	109.34(10)
Cd(1)-S(43)	2.589(1)	N(56)$1- Cd(1)-S(13)	94.77(10)
Cd(1)-N(56)$1	2.279(4)	N(56)$1- Cd(1)-S(43)	117.07(11)
S(11)-C(12)	1.722(5)	N(56)$1- Cd(1)-S(41)	104.57(10)
S(13)-C(12)	1.729(5)	S(11)- Cd(1)-S(41)	104.85(5)
C(12)-N(14)	1.341(5)	S(11)- Cd(1)-S(43)	133.29(5)
S(41)-C(42)	1.714(5)	S(13)- Cd(1)-S(41)	160.65(5)
S(43)-C(42)	1.730(5)	S(13)- Cd(1)-S(43)	101.59(5)
C(42)-N(44)	1.348(5)	S(11)- Cd(1)-S(13)	68.58(5)

$1 symmetry element in **1** 1-x, -y, 1-z in **2** -x, -y, -z

Table S4. Selected bond lengths (Å) and angles (^{0}) for complex **(6).**

Bond lengths/Å		Bond angles/°	
Cd(2) – S(11)	2.733(2)	S(41)–Cd(2)–S(43)	69.95(5)
Cd(2) – S(13)	2.538(2)	S(11)–Cd(2)–S(13)	68.54(5)
Cd(2) – S(41)	2.539(2)	S(73)–Cd(2)–S(41)	107.42(5)
Cd(2) – S(43)	2.648(2)	S(73)–Cd(2)–S(11)	93.73(4)
Cd(2) – S(73)	2.635(1)	S(11)-Cd(2)–S(41)	102.89(5)
Cd(1) – S(71)	2.585(1)	S(73)–Cd(2)–S(43)	103.37(5)
Cd(1) – S(73)	2.681(1)	S(73)–Cd(2)–S(13)	107.19(5)

Cd(1) – S(11)	2.914(1)	S(11)–Cd(2) –S(43)	162.74(5)
N(14) – C(12)	1.338(6)	S(13)–Cd(2) –S(41)	144.79(6)
C(12) – S(11)	1.736(6)	S(13)–Cd(2) –S(43)	107.78(6)
C(12) – S(13)	1.707(6)	Cd(1)–S(11)–Cd(2)	85.33(4)
C(42) – N(44)	1.351(8)	S(71)–Cd(1)–S(73)	68.86(4)
S(41) – C(42)	1.713(6)	S(71)–Cd(1)–S(11)	91.33(4)
S(43) – C(42)	1.708(7)	S(11)–Cd(1)–S(73)	88.77(4)
S(71) – C(72)	1.713(5)	Cd(1)–S(73)–Cd(2)	92.17(4)
S(73) – C(72)	1.756(5)		
N(74) –C72)	1.327(6)		

Table S5. Hydrogen bonds /Å, in complex **5.**

D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°	Symmetry element of acceptor atom
N34-H34···O1	0.86	2.10	2.958(8)	178	1-x,1-y,2-z
N64-H64···N26	0.86	2.07	2.923(6)	168	1+x,y,-1+z
C2-H2C···S13	0.96	2.97	3.751(4)	139	x,y,-1+z

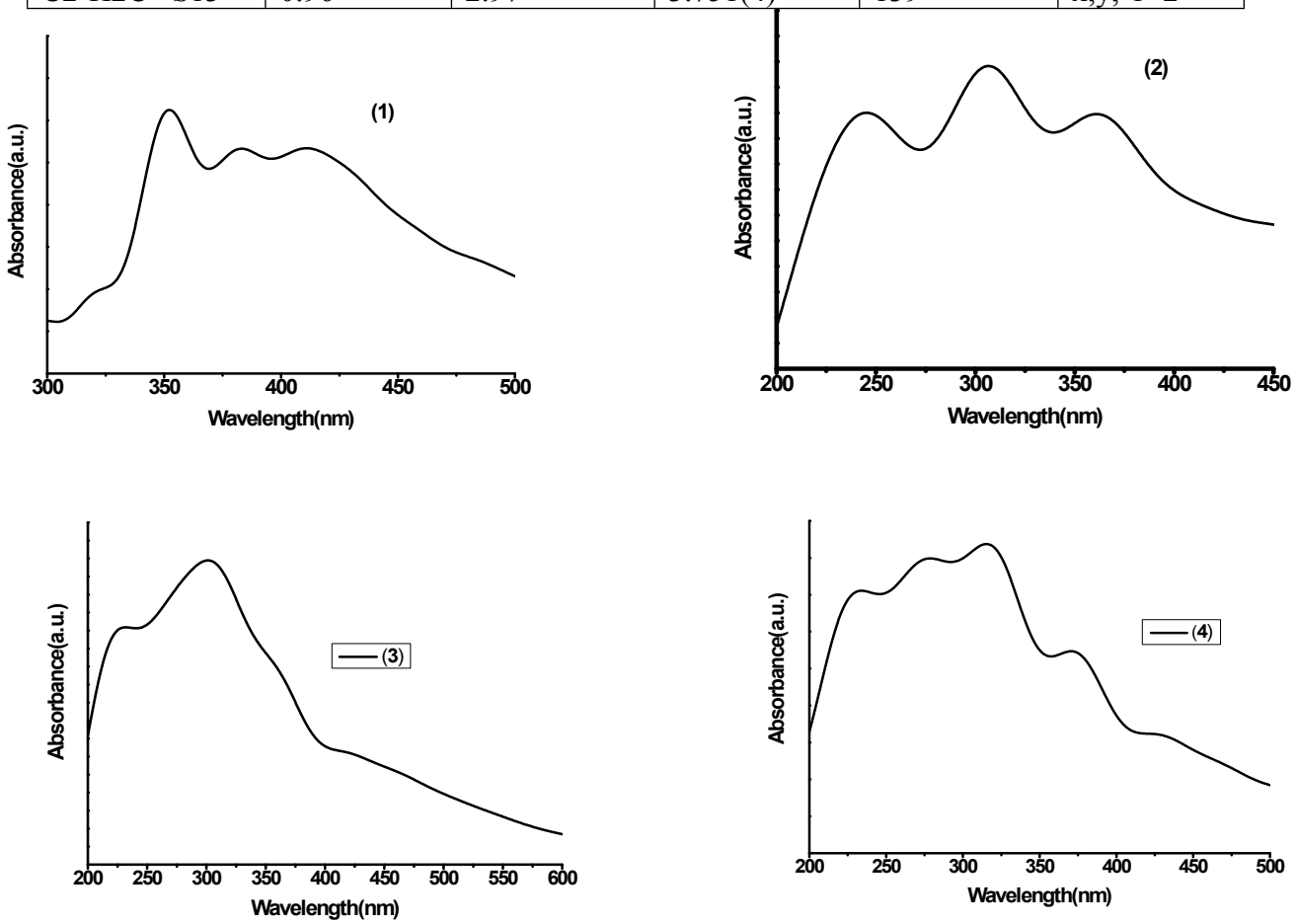


Fig. S1 UV-Vis. spectra of complexes as nujol mull (**1-4)**

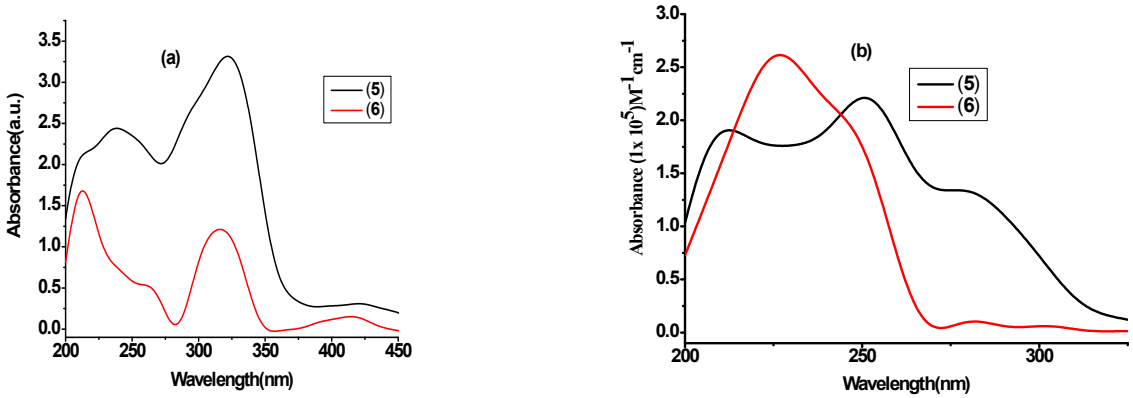


Fig. S2 UV-Vis. spectra of **5** and **6** (a) as nujol mull (b) in 10^{-5} DMSO.

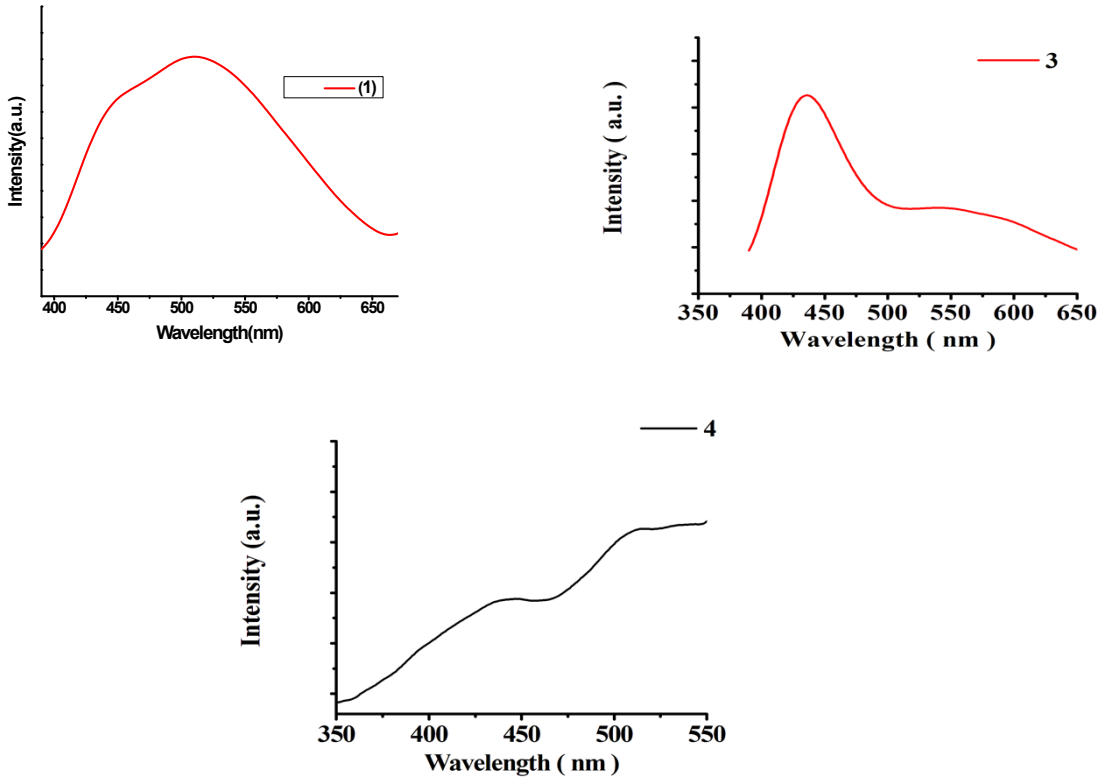


Fig. S3a Photo luminescent spectra in solid state (**1**, **3** and **4**) (λ_{ex} ~ 400-410 nm)

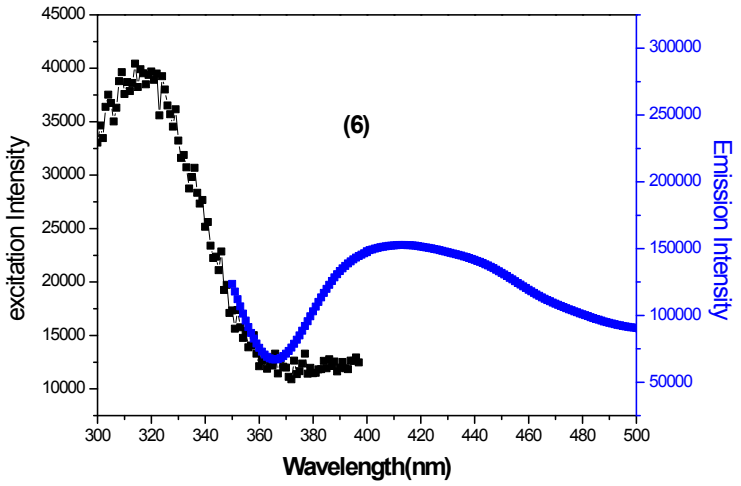


Fig. S3b Photo luminescent spectra in solid state of **6**.

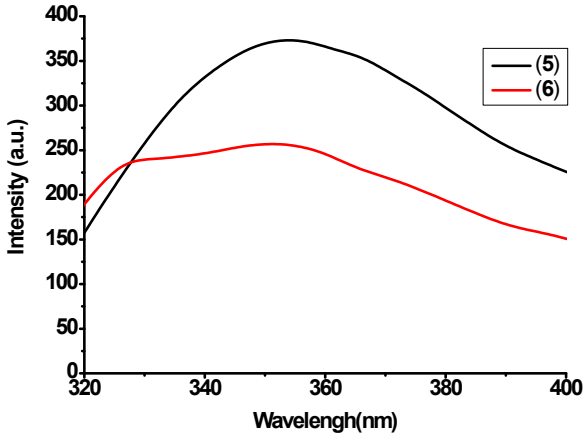


Fig. S4 Photo luminescent spectra in solution (**5** and **6)** at room temperature (λ_{ex} = 300 nm)

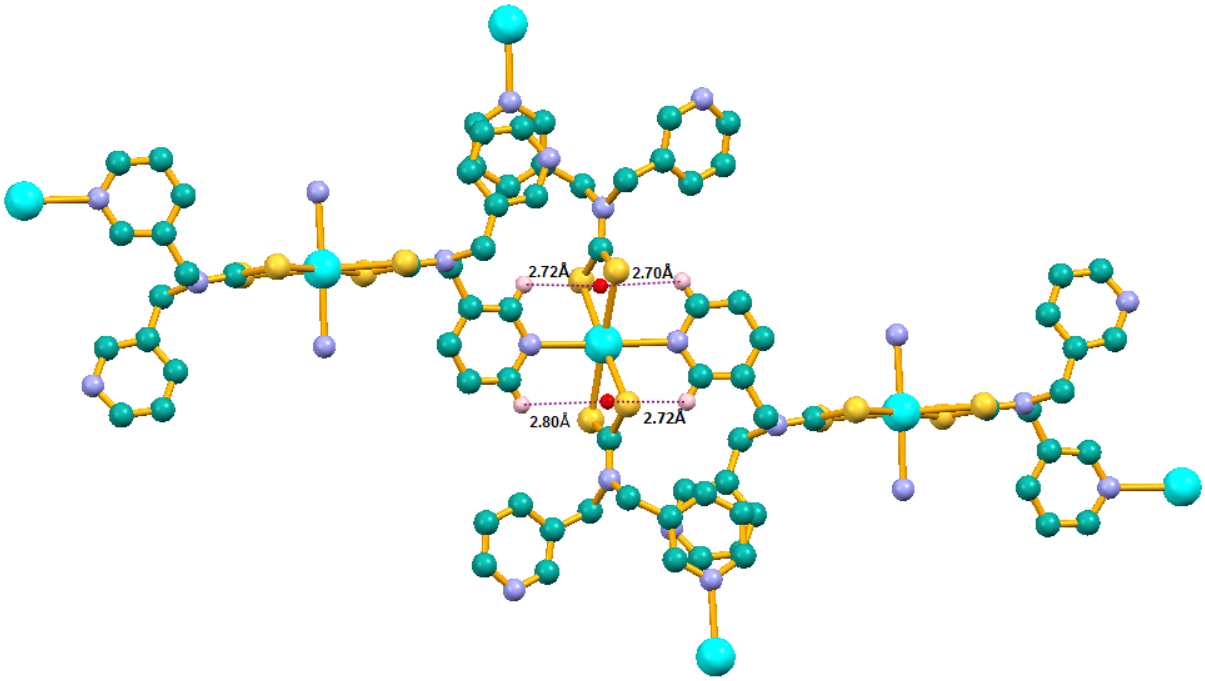


Fig. S5 supramolecular structure of **2** sustained by the C-H···π (chelate = CdS_2C) interactions

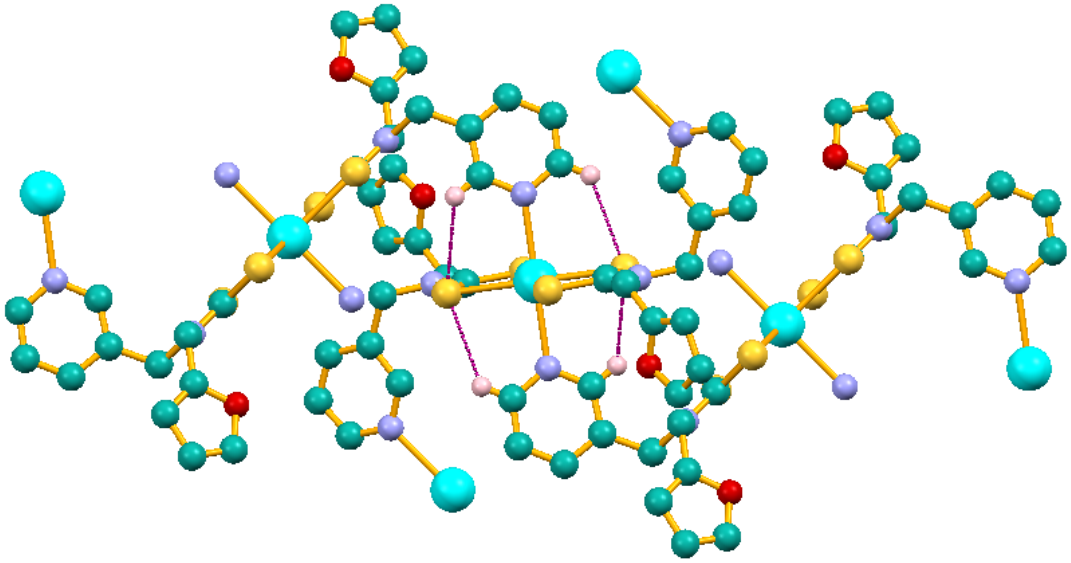


Fig. S6 View of C-H…S interactions in **3** deviating from 2-D plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)**.**

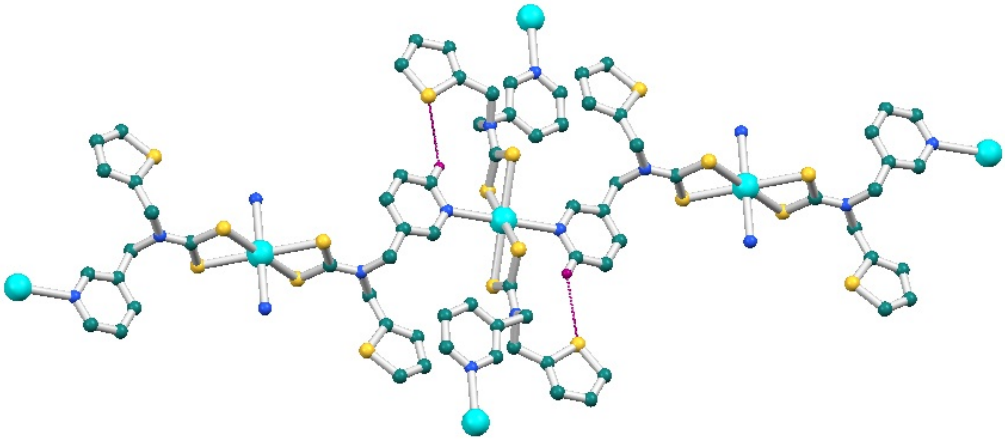


Fig. S7 View of C-H…S interactions to stabilized complex **4** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)**.**

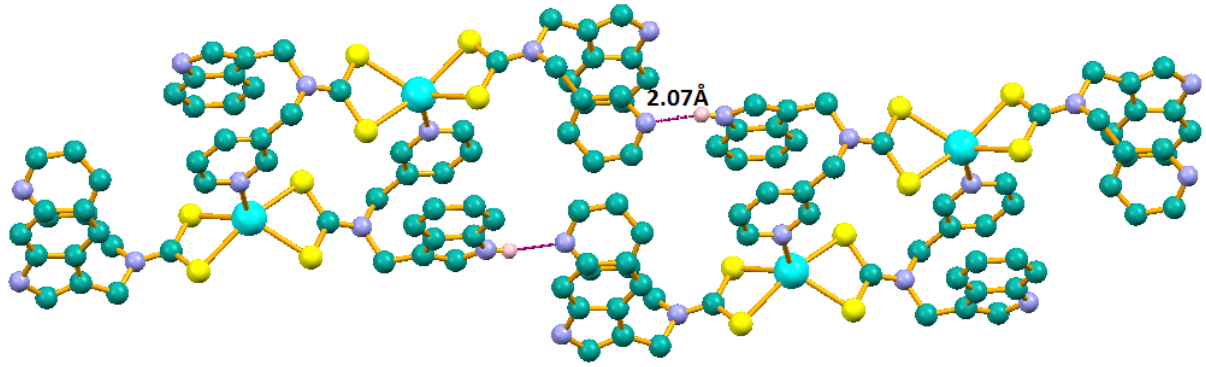


Fig. S8 View of the 1-D chain motifs for **5** along the *b* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

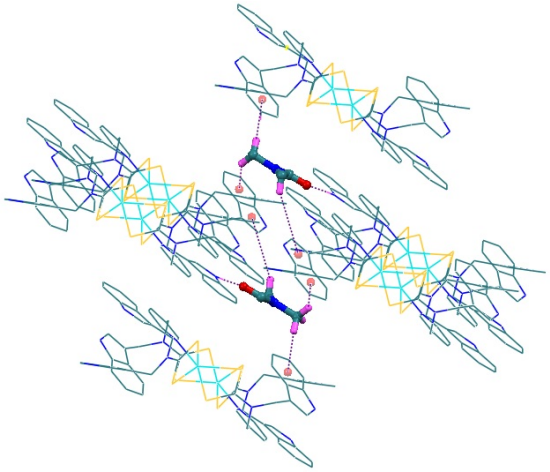


Fig. S9 C –H···π interactions between solvent and complex leading to 3-D supramolecular chain in **5**.

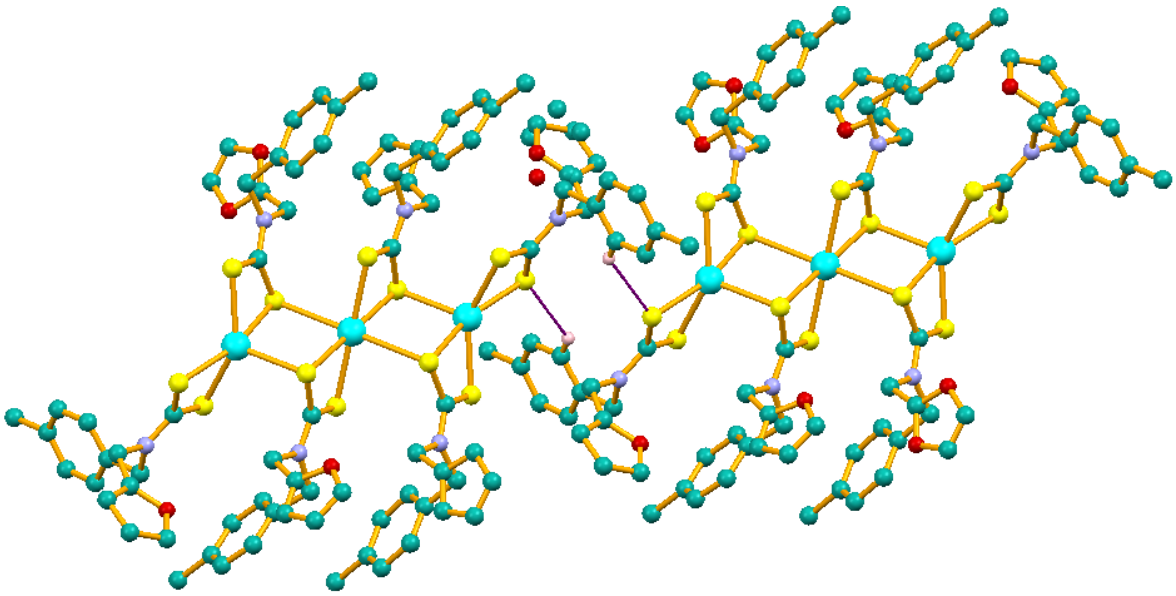


Fig. S10 supramolecular structure is stabilised through C-H···S hydrogen bonding interactions

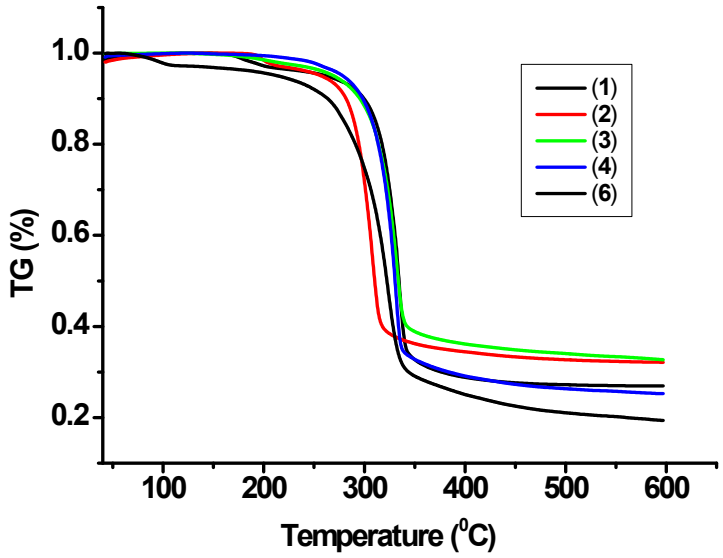


Fig. S11 Superimposed thermogravimetric (TG) trace of the complexes.

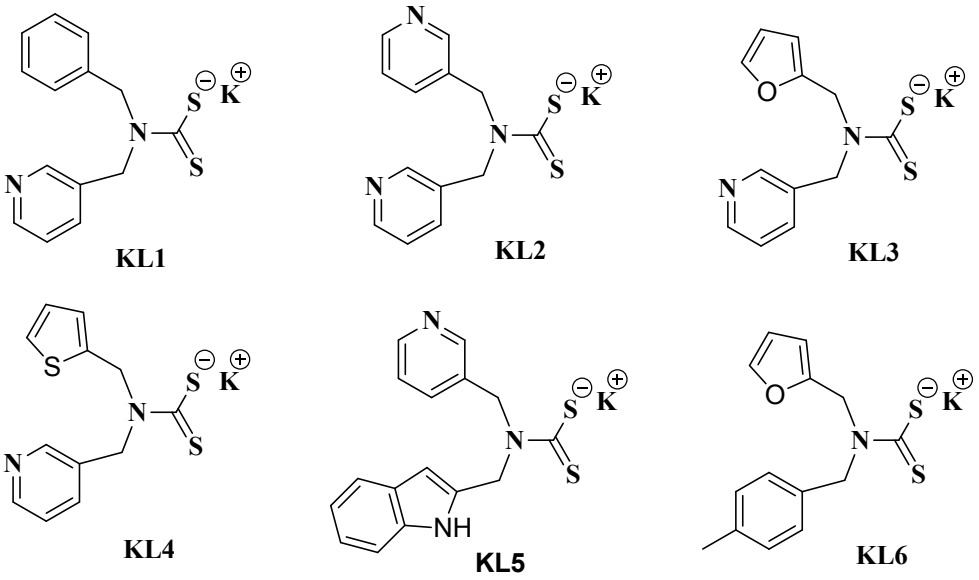
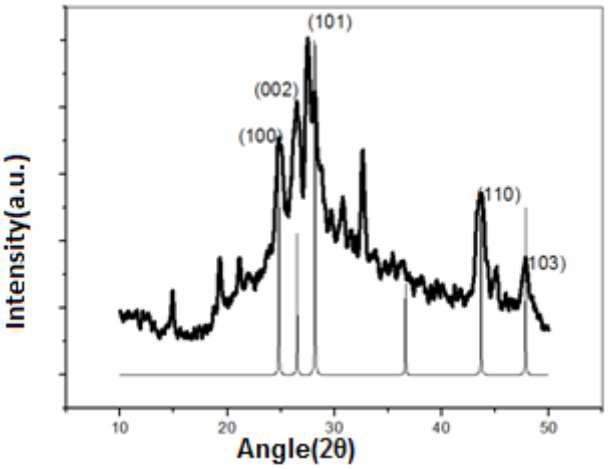
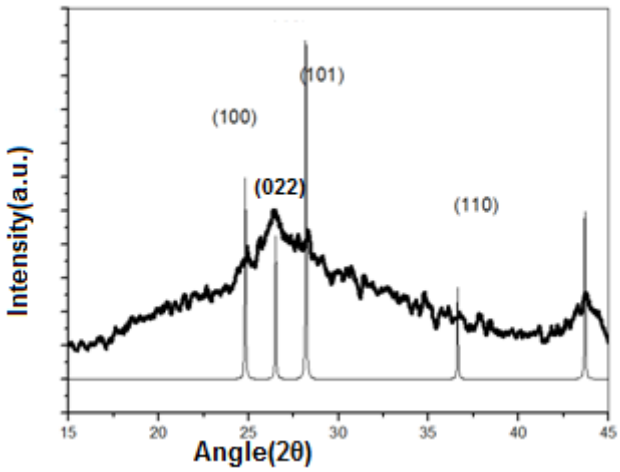


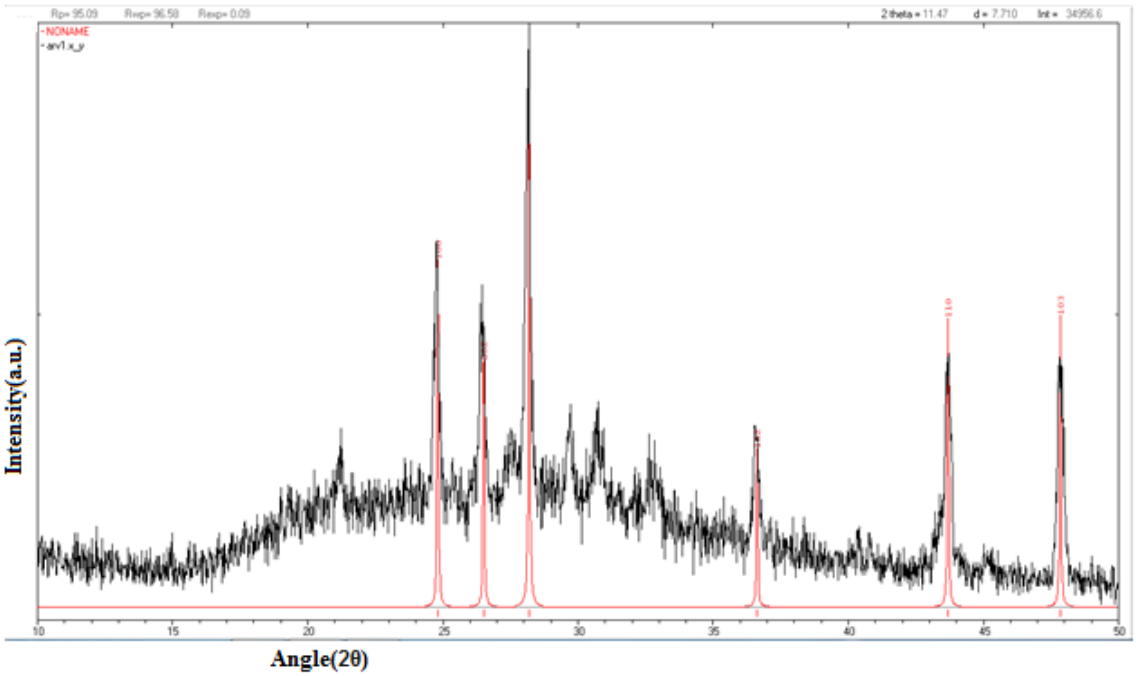
Fig. 12 Structures of the potassium salt of the ligands used in this work.



(a)



(b)



(c)

Fig. S13 PXRD patterns of TGA product (CdS) of **1**, **2** and **6** in a, b and c respectively.

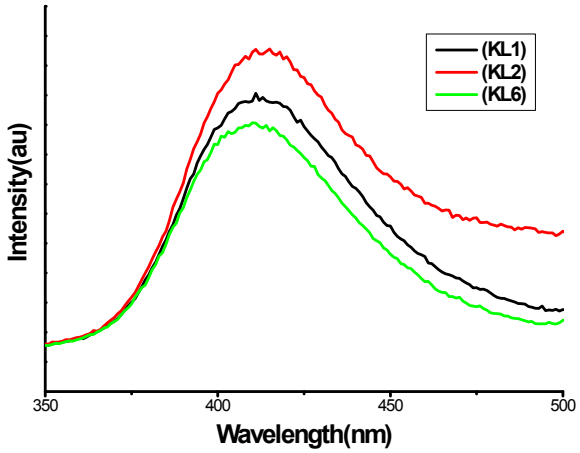


Fig. S14 Photoluminescent spectra of ligands in solid state (λ_{ex} = 280 nm)