Supporting Information

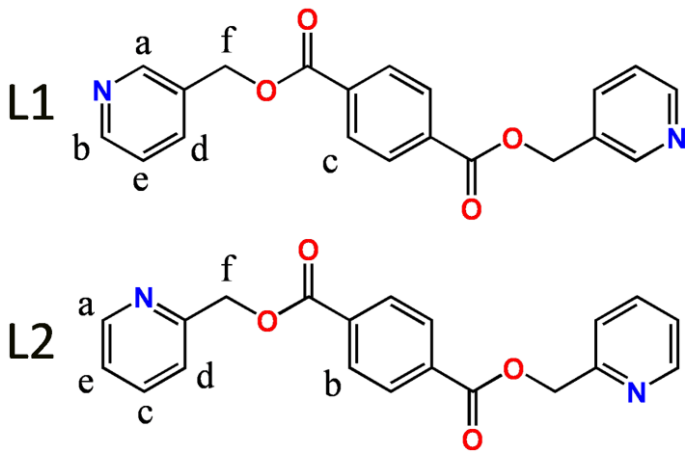
Structural Modulation, Argentophilic Interactions and Photoluminescence Properties of Silver(I) Coordination Polymers with Isomeric N-donor Ligands

Kamal Kumar Bisht[a], Amal Cherian Kathalikkattil[a,b] and Eringathodi Suresh[a]*

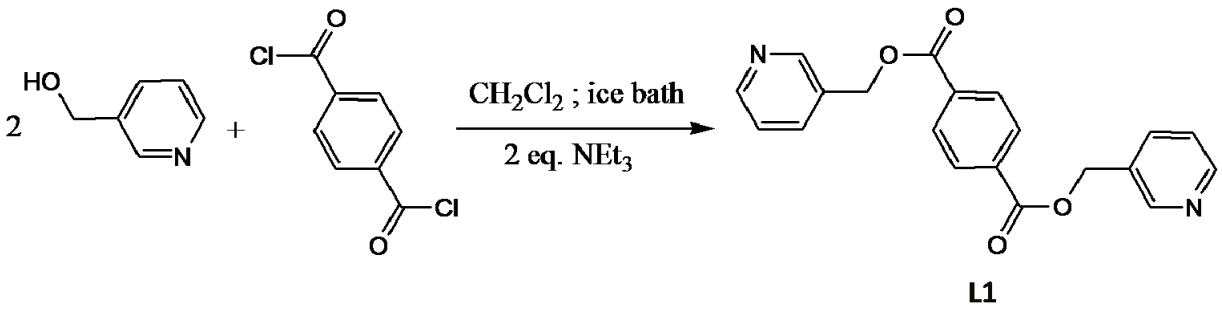
[a]Analytical Discipline and Centralized Instrument Facility, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR) G.B.Marg, Bhavnagar -364 002, Gujarat, India.

[b]Department of Chemical Engineering, Pusan National University, Jangjun-Dong, Gumjung-gu, Busan, 609-735, Republic of Korea.

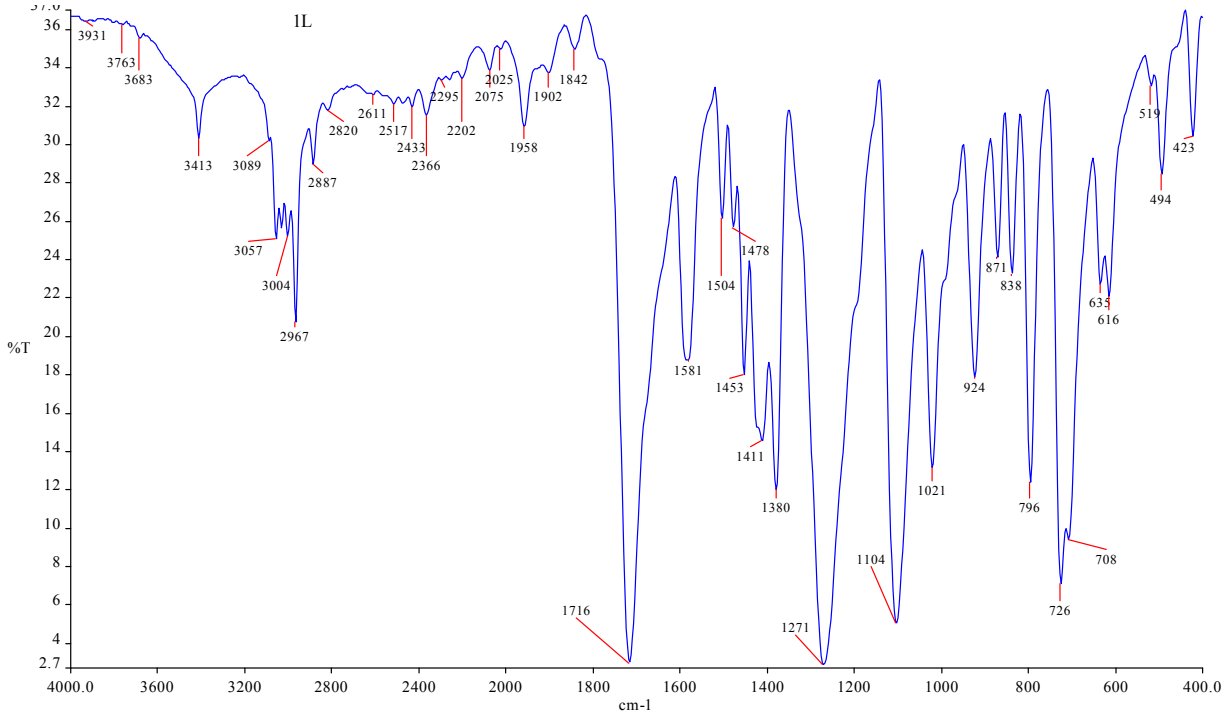
E-mail: esuresh@csmcri.org and sureshe123@rediffmail.com



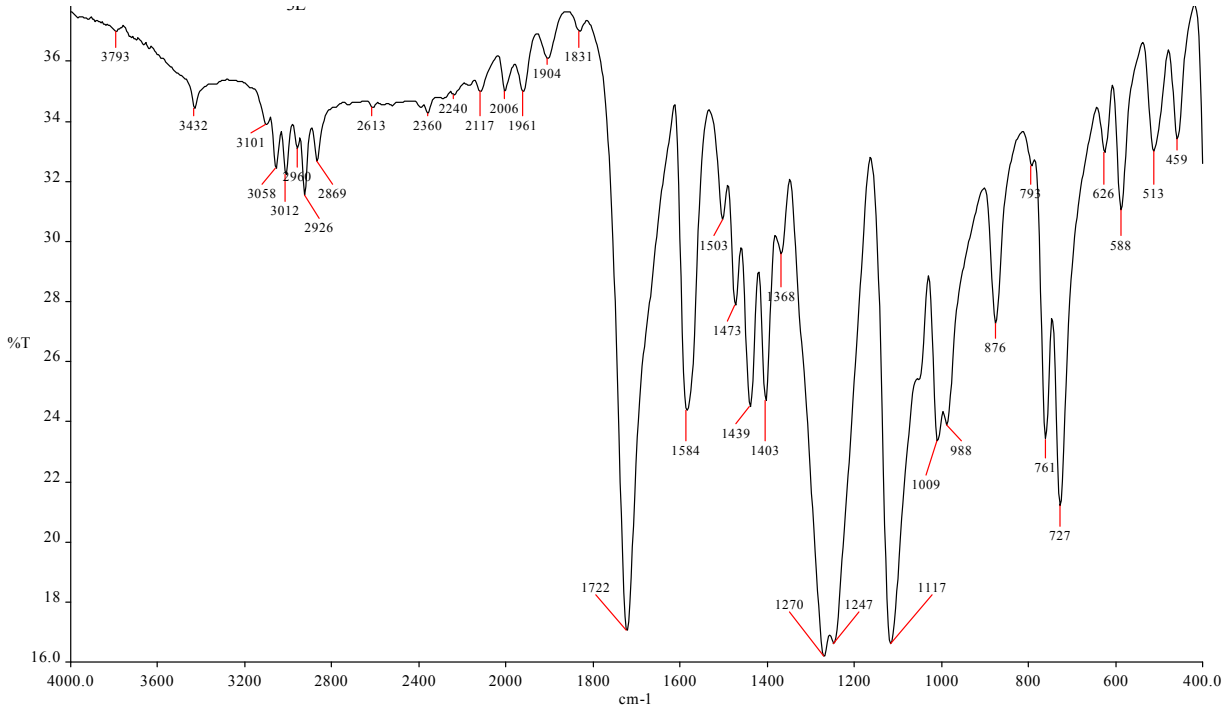
Scheme S1. Chemical structures of linkers bis(pyridine-3-ylmethyl)terephthalate (**L1**) and bis(pyridine-2-ylmethyl)terephthalate (**L2**). Lowercase alphabets are given to indicate the respective protons in nmr spectra.



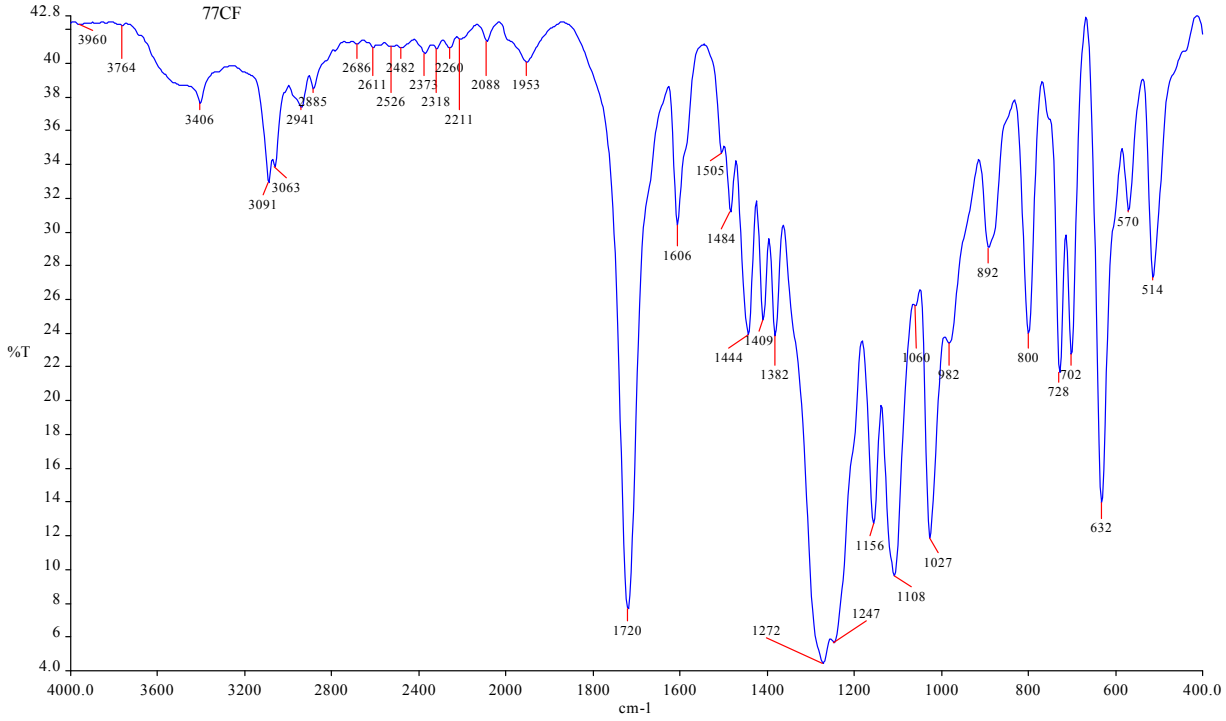
Scheme S2. Synthetic procedure to prepare bis(pyridine-3-ylmethyl)terephthalate (**L1**).



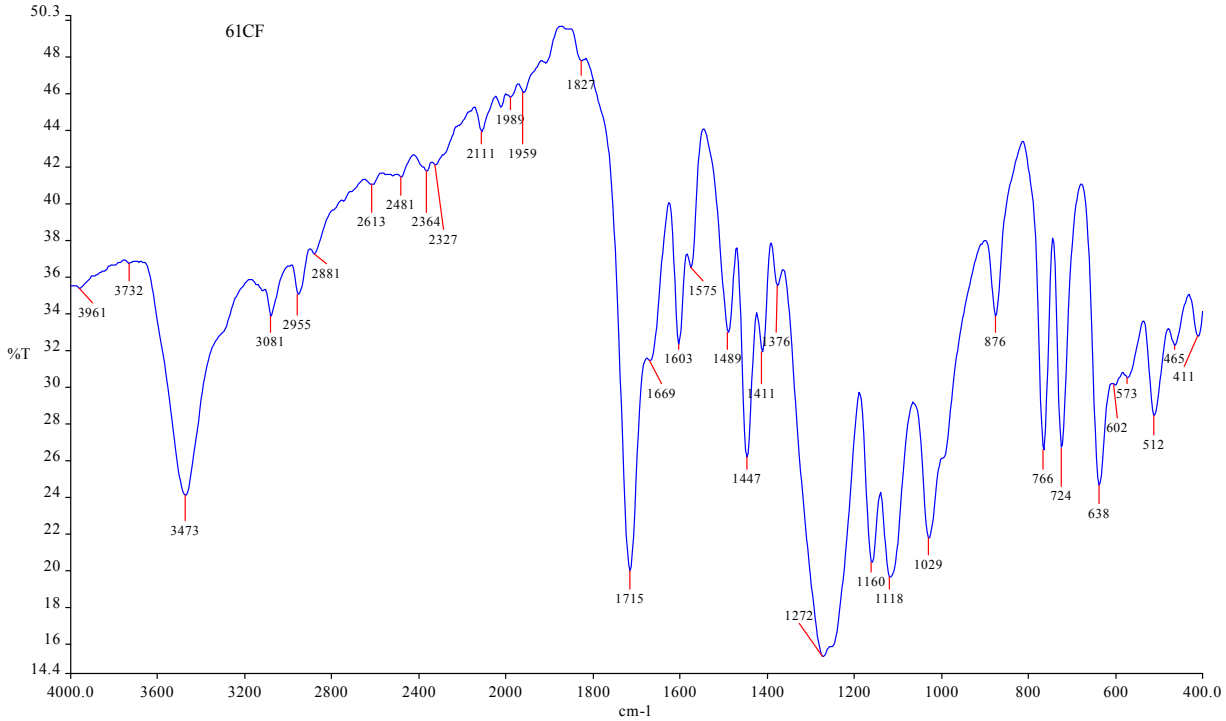
S3: FTIR spectra for compound bis(pyridine-3-ylmethyl)terephthalate (**L1**)



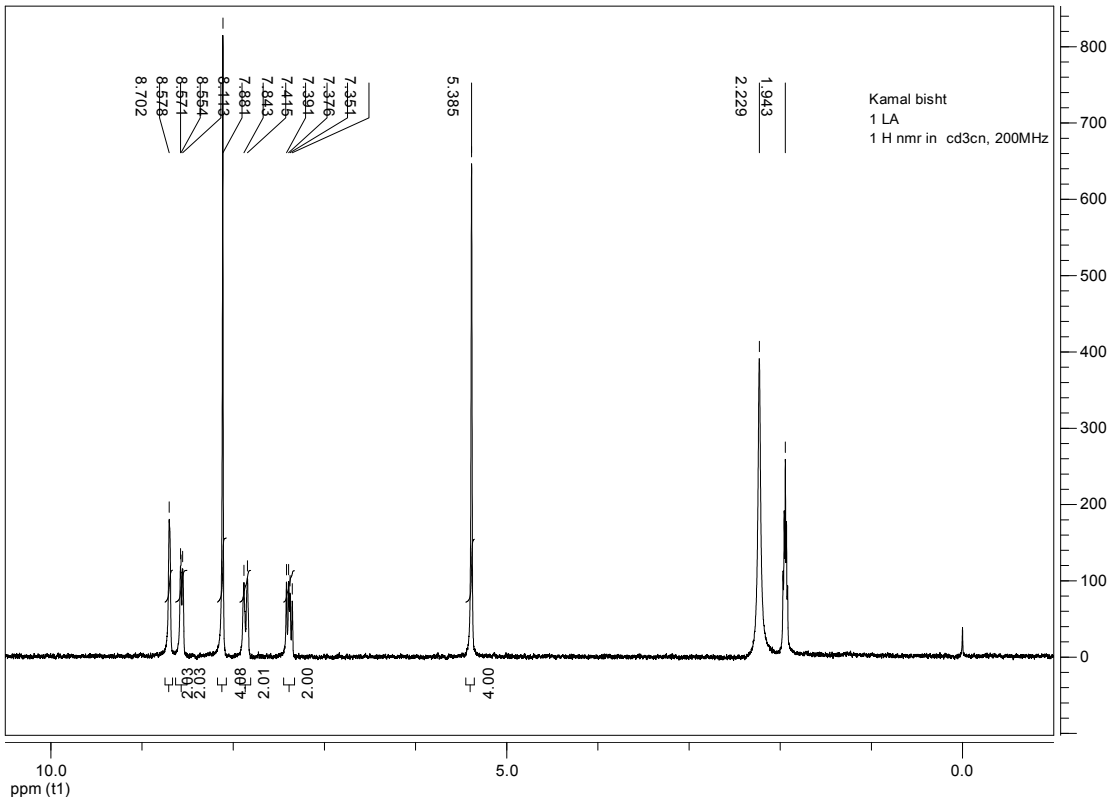
S4: FTIR spectra for compound bis(pyridine-2-ylmethyl)terephthalate (**L2**)



S5: FTIR spectra for coordination polymer **1**



S6: FTIR spectra for coordination polymer **2**



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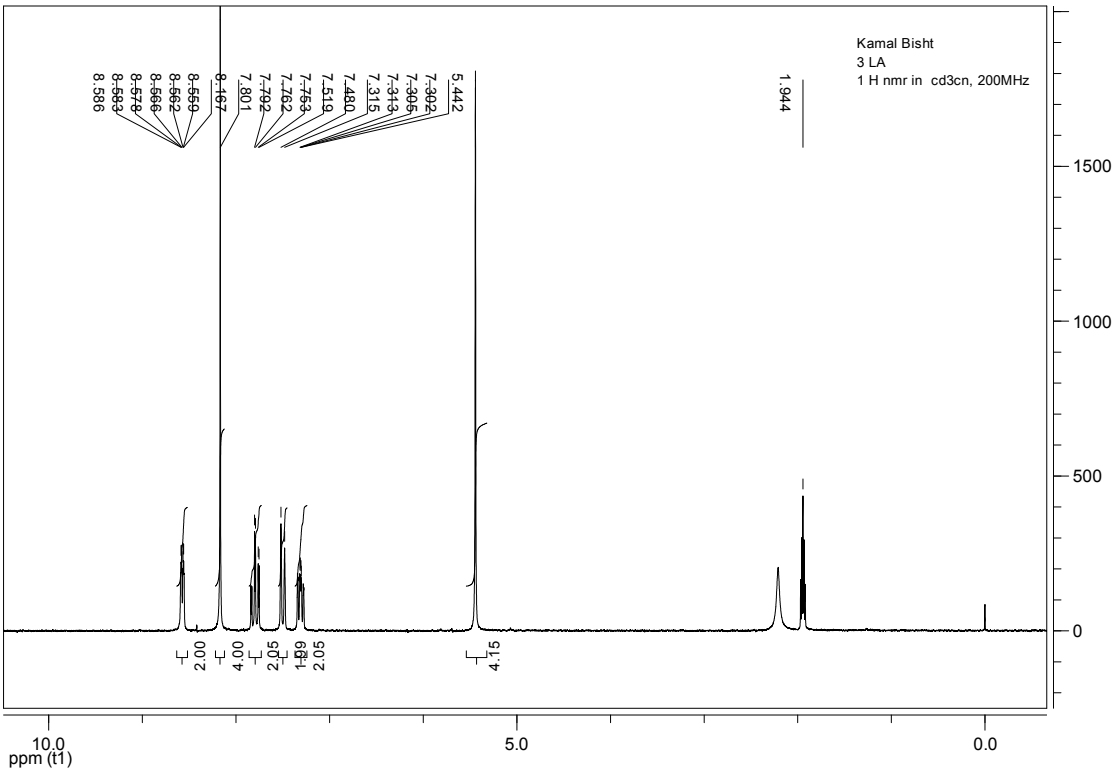
33 **S7:** ^{1}H NMR spectra for **L1** in *d3*-acetonitrile



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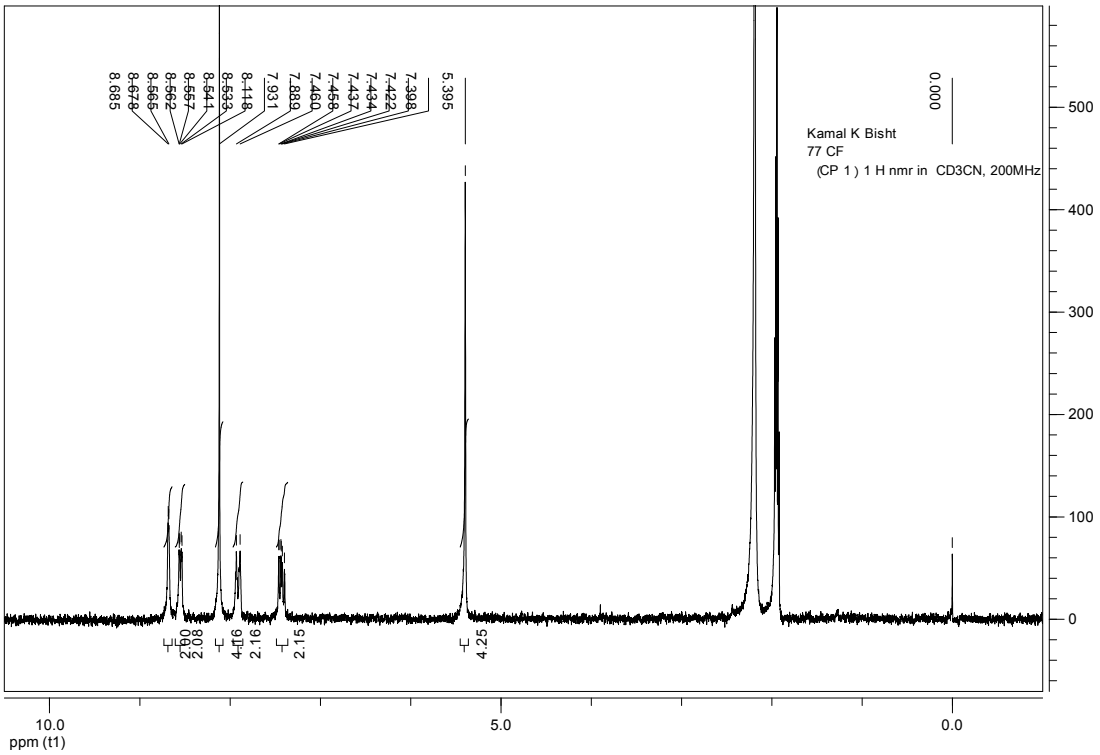
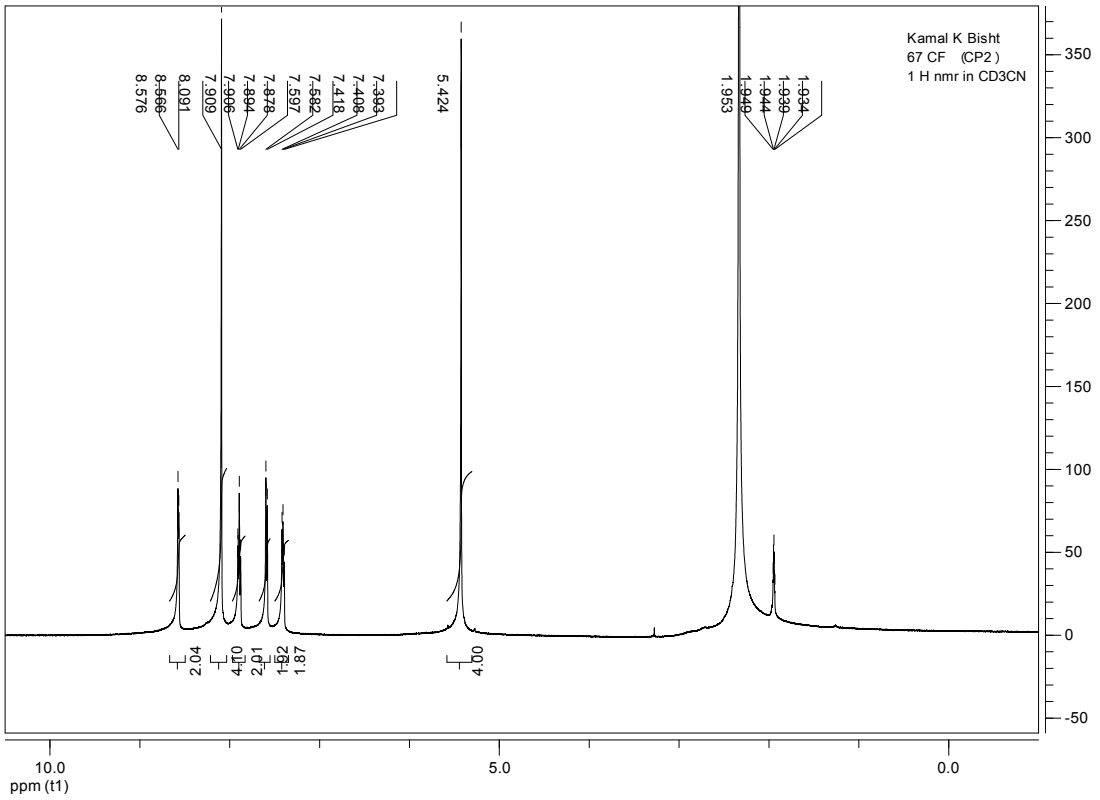
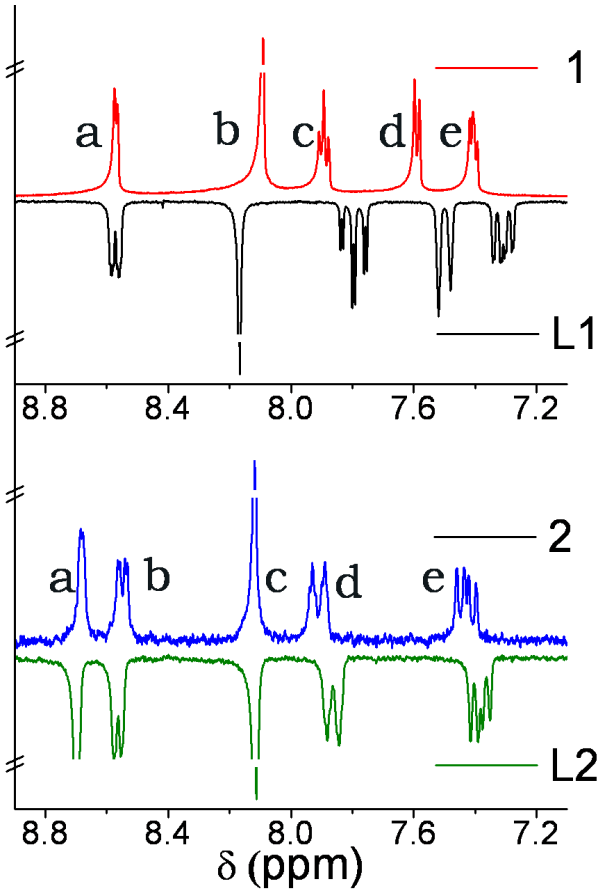
35 **S8:** ^{1}H NMR spectra for **L2** in *d3*-acetonitrile



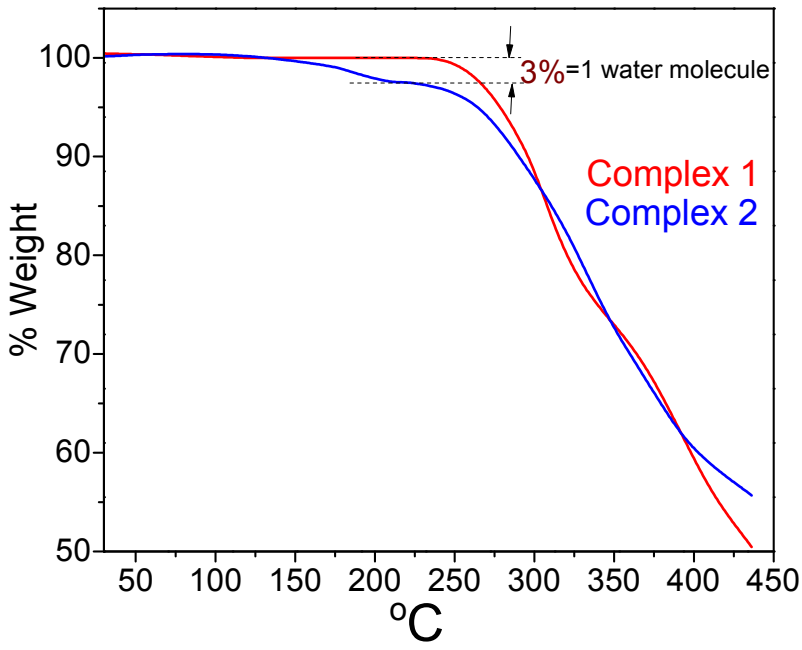
S9: ^{1}H NMR spectra for **1** in *d3*-acetonitrile



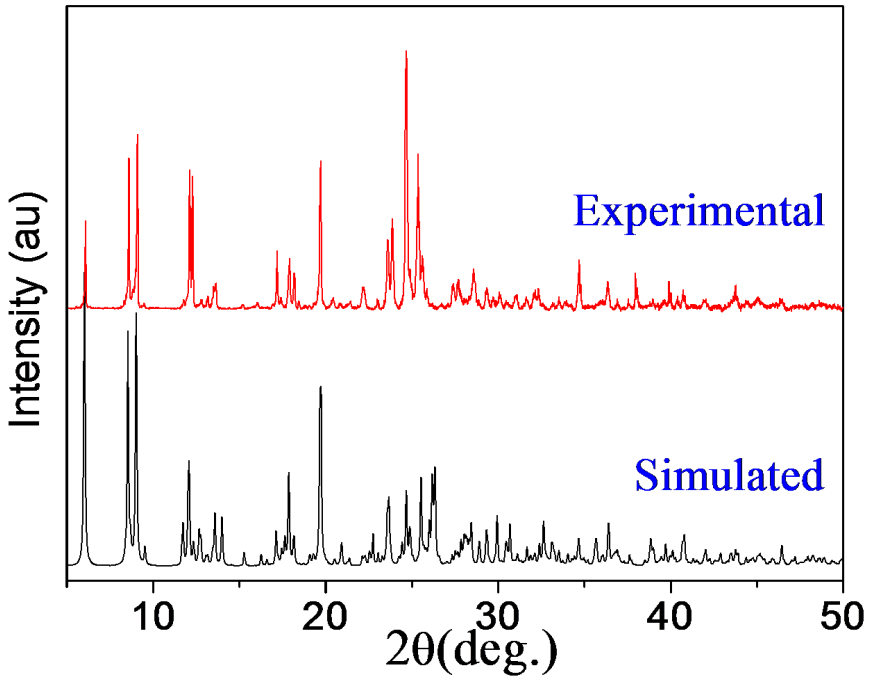
S10: ^{1}H NMR spectra for **2** in *d3*-acetonitrile



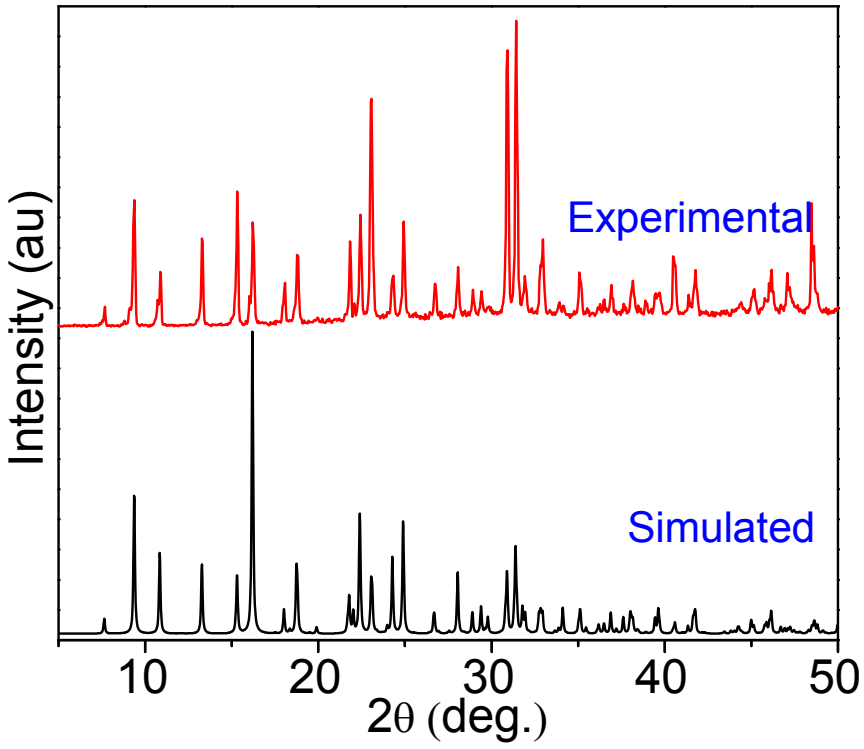
S11: Aromatic region of ^{1}H nmr spectra for complexes **1** and **2**. The ^{1}H nmr spectra of respective ligands are also given as reflection to show the shifting in pyridyl proton positions after complexation. a-e represents the pyridyl protons as shown in scheme **S1**.



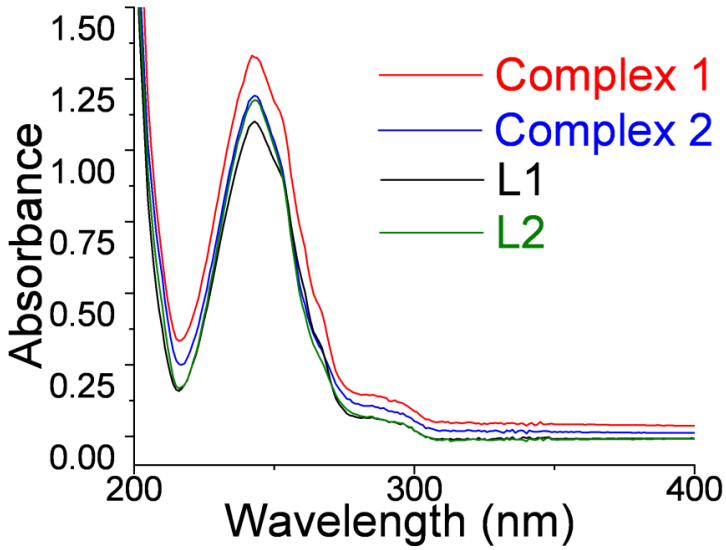
S12: TGA profiles of coordination polymers **1** and **2**



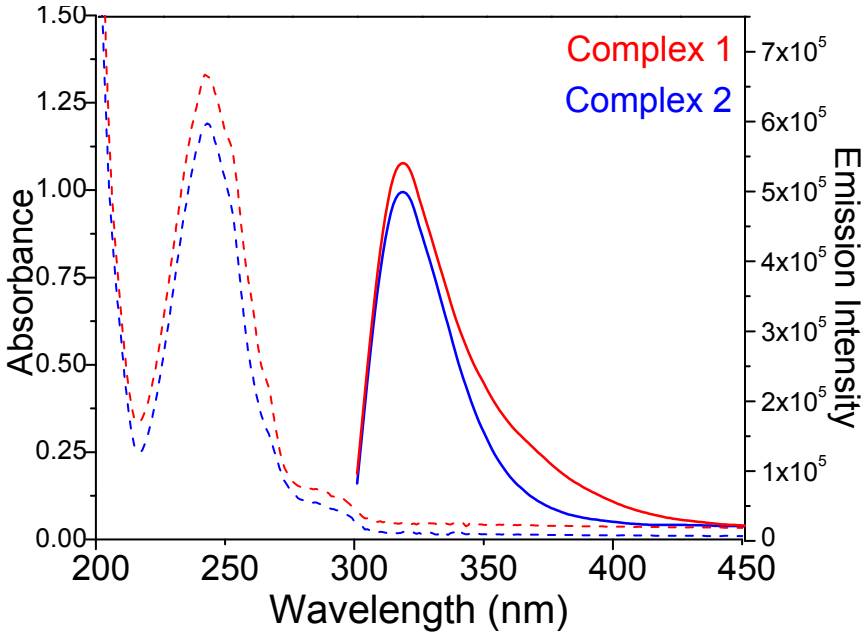
S13: Comparison of experimental and simulated XRPD profiles of complex **1**



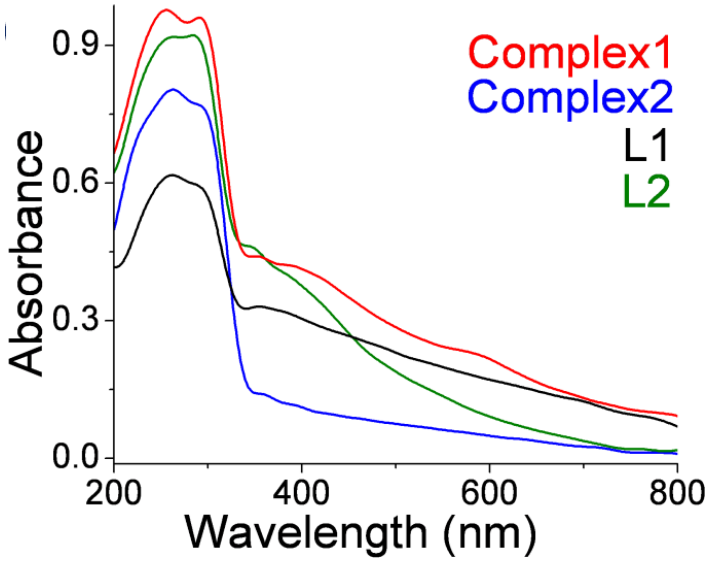
S14: Comparison of experimental and simulated XRPD profiles of complex **2**



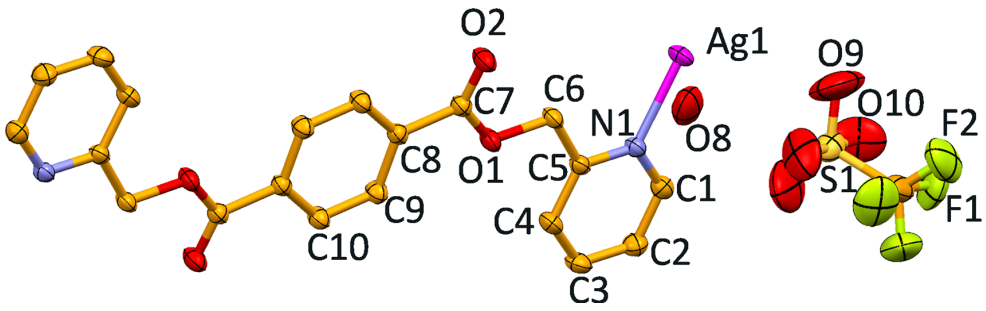
S15: Absorption spectra of compounds **1**, **2**, **L1** and **L2** in acetonitrile solutions (~1x10^{-4} M) at ambient temperature.



S16: Luminescence spectra of coordination polymers **1** and **2** in acetonitrile solutions (~1x10^{-4} M) at ambient temperature. Absorption profiles are given as dotted plots for the sake of comparison.



S17: Absorption spectra of compounds **1**, **2**, **L1** and **L2** in solid state at ambient temperature recorded using crystalline powder samples prepared by gentle crushing of crystals.



S18: ORTEP diagram of **2** with atom numbering scheme (40% probability factor for the thermal ellipsoids).

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75 **Table S1:** Crystal Data and Refinement Parameters for Compound **L1, L2, Complex 1** & **2**

Identification code	**L1**	**L2**	**Complex 1**	**Complex 2**
Chemical formula	$C_{20}H_{16}N_2O_4$	$C_{20}H_{16}N_2O_4$	$C_{44}H_{35}Ag_2F_6N_5O_{14}S_2$	$C_{21}H_{18}Ag_1F_3N_2O_8S_1$
Formula weight	348.35	348.35	1251.63	623.30
Crystal Colour	Colourless	Colourless	Colourless	Colourless
Crystal Size (mm)	0.61 x0.30 x0.15	0.33 x 0.23 x 0.05	0.28 x 0.14 x 0.08	0.40 x 0.33 x 0.04
Temperature (K)	100(2)	293(2)	110(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space Group	$P2_1/n$	$P2_1/c$	P-1	Pbcn
a(Å)	5.6023(9)	7.831(3)	11.2497(7)	5.9957(11)
b(Å)	16.038(2)	8.838(3)	14.6138(8)	23.128(4)
c(Å)	9.1681(14)	12.436(4)	15.2418(9)	16.303(3)
α(°)	90	90	85.752(2)	90
β(°)	97.593(3)	93.886(7)	73.7830(10)	90
γ (°)	90	90	72.581 (3)	90
Z	2	2	2	4
V(Å^3)	816.5(2)	858.7(5)	2295.6(2)	2260.7(7)
Density (Mg/m^3)	1.417	1.347	1.811	1.831
Absorption Coefficient(mm^{-1})	0.100	0.095	1.043	1.061
F(000)	364	364	1252	1248
Reflections Collected	4862	5928	19515	12013
Independent Reflections	1906	1508	10313	2475
$R_{(int)}$	0.0335	0.0537	0.0181	0.0243
Number of parameters	150	150	654	178
S(Goodness of Fit) on F^2	1.247	1.119	1.032	1.093
Final R1/wR2 (I>2σ(I)	0.0681/ 0.1606	0.0739 / 0.1442	0.0396/ 0.1077	0.0433/ 0.1057
Weighted R1/wR2(all data)	0.0820/0.1766	0.1239 / 0.1645	0.0418/ 0.1094	0.0516/ 0.1106
CCDC Number	868386	868387	868388	868389

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Table S2. Hydrogen Bonding Table for **Complex 1** and **Complex 2**

Complex 1			
D-H...A	**d(H...A) (Å)**	**d(D...A) (Å)**	**∠ D-H…A (°)**
C(1)–H(1)…..Ol(14)[1]	2.45	3.183(3)	136
C(3)–H(3)….O(3)[2]	2.38	3.215(3)	149
C(5)–H(5)...O(10)[3]	2.43	3.272(5)	150
C(6)–H(6A)...O(3)[2]	2.57	3.234(3)	126
C(15)–H(15B)....O(2)[3]	2.59	3.348(3)	135
C(20)–H(20)....O(12) [3]	2.58	3.485(4)	164
C(21)–H(21)....O(9) [3]	2.38	3.160(4)	141
C(30)–H(30). ..O(11)[1]	2.60	3.199(5)	123
C(33)–H(33). ..O(12)[1]	2.35	3.237(3)	160
C(38)–H(38). ..O(13)[4]	2.54	3.378(4)	150
C(43)–H(43A). ..O(11)[5]	2.53	3.320(10)	139
Symmetry code : 1. x,y,-1+z 2. 1+x,y,z 3. -1+x,y,z 4. 2-x,-y,-z 5. x, y, z			
Complex 2			
D-H...A	**d(H...A) (Å)**	**d(D...A) (Å)**	**∠ D-H…A (°)**
O(8)-H(8C)...Ol(10)[1]	2.07(6)	2.701(9))	151(7)
C(6)-H(6A)...O(8)[1]	2.51	3.413(8)	154
C(6)-H(6B)...O(2)[2]	2.47	3.317(4)	146
Symmetry code : 1. x,y,z 2.1-x, y, 3/2-z			

Table. S3: Selected Bond Lengths(Å) and Angles(º) for Complexes **1 and 2**

Complex 1			
Ag(1)-Ag(2)	3.3642(4)	F(4)-C(42)	1.339(3)
Ag(1)-N(1)	2.169(2)	F(5)-C(42)	1.330(4)
Ag(1)-N(2)$^{\#1}$	2.168(2)	F(6)-C(42)	1.341(4)
Ag(2)-N(3)	2.186(2)	S(1)-O(9)	1.430(2)
Ag(2)-N(4)$^{\#2}$	2.190(2)	S(1)-O(10)	1.423(3)
Ag(2)-N(5)	2.716(3)	S(1)-O(11)	1.397(3)
Ag(1)-O(14)	2.620 (4)	S(1)-C(41)	1.815(4)
N(5)-C(44)	1.376(4)	S(2)-O(12)	1.438(2)
F(1)-C(41)	1.346(5)	S(2)-O(13)	1.431(3)
F(2)-C(41)	1.312(4)	S(2)-O(14)	1.445(2)
F(3)-C(41)	1.282(5)	S(2)-C(42)	1.818(3)
N(2$^{\#1}$-Ag(1)-N(1)	161.93(9)	N(4)$^{\#2}$-Ag(2)-Ag(1)	80.86(6)
N(2$^{\#1}$-Ag(1)-Ag(2)	93.58(6)	N(3)-Ag(2)-N(5)	89.83(9)
N(1)-Ag(1)-Ag(2)	104.43(6)	N(4)$^{\#2}$-Ag(2)-N(5)	94.04(9)
N(3)-Ag(2)-N(4)$^{\#2}$	174.21(9)	Ag(1)-Ag(2)-N(5)	133.80(6)
N(3)-Ag(2)-Ag(1)	93.35(6)		
Symmetry transformations: $^{\#1}$ x+1,y,z-1 ; $^{\#2}$ x-1,y,z+1			
Complex 2			
Ag(1)-N(1) $^{\#1}$	2.149(3)	S(1)-O(9)$^{\#1}$	1.292(6)
C(11)-F(2)$^{\#1}$	1.216(6)	S(1)-O(10)$^{\#1}$	1.546(12)
C(11)-F(1)$^{\#1}$	1.575(9)	S(1)-C(11)	1.737(9)
N(1)$^{\#1}$-Ag(1)-N(1)	175.57(14)	O(1)-C(6)-C(5)	108.4(2)
C(1)-N(1)-Ag(1)	117.0(2)	C(7)-O(1)-C(6)	116.4(2)
C(5)-N(1)-Ag(1)	124.5(2)	O(1)-C(7)-C(8)	112.0(3)
Symmetry transformations: $^{\#1}$.-x,y,-z+3/2			