

Supporting Information

Anion and Guest Directed Tetracyclic Macrocycles of Ag₅L₄ and Ag₆L₄ with an Arc-shaped Ligand Containing Pyridine and Benzimidazole Units: Reversal of Anion Selectivity by Guest

Avishek Dey and Kumar Biradha*

E-mail: kbiradha@chem.iitkgp.ernet.in

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General experimental details:

All the chemicals such as *o*-phenylenediamine, pyridine-3,5-dicarboxylic acid, polyphosphoric acid (PPA), methyl iodide, silver salts were purchased from local chemical suppliers or Sigma Aldrich and used without purification with the exception of tetrahydrofuran (THF), which was dried over sodium and benzophenone before using.

X-ray Powder diffraction (XRPD) data were recorded with a Bruker D8-advance diffractometer at room temperature. ¹H NMR (400/600 MHz) spectra were recorded on a BRUKER-AC 400/600 MHz spectrometer. FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Thermal gravimetric analysis was carried out with a Red croft 870 thermal analyzer (PerkinElmer). The complexes were used under nitrogen atmosphere at heating rate 10°C min⁻¹. MALDI-TOF experiment was carried out by a BRUKER ULTRAFLEXTRME MALDI TOF mass spectrometer. The solid state luminescence spectra were collected with a Spex Fluorolog-3 (model FL3-22) spectrofluorimeter.

Synthesis of L:

The ligand **L** was synthesized using the reported procedure by us. Pyridine-3,5-dicarboxylic acid (3.0 g, 17.96 mmol) and *o*-phenylenediamine (3.879 g, 35.92 mmol) were added to polyphosphoric acid (PPA) and mixed thoroughly to make a paste. The mixture was then heated slowly to 180-200 °C and stirred for 3-4 h; the mixture was allowed to cool to about 100 °C. The resultant green colored viscous crude mixture was poured into a large volume of rapidly stirred cold water and it was neutralized with an aqueous ammonia solution to make the solution slightly basic. The insoluble residue was collected by filtration and washed with water until the residue part became base free. The product was dried under vacuum and recrystallized from hot methanol. The crystalline powder was isolated with a good yield (70%). mp > 300°C.

1.158 g of sodium hydride (95%) was added to a stirred dry THF solution (40 mL) of above compound (3.0 g, 9.6 mmol) in a 100 ml round bottom flask, under a nitrogen atmosphere, over 30 min through a side arm. Methyl iodide (2.72 g, 19.2 mmol) was added to this solution drop wise. The reaction mixture was stirred overnight, quenched with water and then poured into 400 mL of water. After stirring the solution for 30 min, a pale yellow precipitate was collected by filtration, washed repeatedly with water and dried in a vacuum for 24 h. The crude product was recrystallized from methanol and kept for slow evaporation at room temperature. After two days, the ligand **L** was collected *via* filtration with a good yield (85%). mp 244°C. ¹H-NMR of **L** in D₆-DMSO: δ 9.22 (s, 2H), δ 8.72 (s, 1H), δ 7.77 (d, 4H), δ 7.38-7.29 (d, 4H), δ 4.01 (s, 6H).

General procedure for the preparation of silver complex: In a 20 ml test tube, silver salt (0.0294 mmol) solution in MeOH (2 ml) was layered on top of MeOH/ CH₂Cl₂ (3 ml, in 2:1 ratio) or MeOH/ CH₂Cl₂/ Guest (3 ml, in 1:1:1 ratio) solution of ligand (0.0294 mmol) placing a blank solution of MeOH/ CH₂Cl₂ (4 ml, in 3:1 ratio) or MeOH/ Guest (4 ml, in 3:1 ratio) in between. The test tube was

covered by aluminium foil and left at room temperature. After 15 days colorless crystals of respective complexes were isolated. Yield~ 50-70 %.

Crystal structure determinations by Single crystal X-ray

All of the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at temperature (273 K or 150 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F² using SHELX-2014.¹ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. The anions in **3-6** & **8** and solvent molecules in **2-8** could not be located and refined; therefore the final refinement was done using PLATON squeeze option.²

Table 1. Crystallographic parameters for complexes 1-8

	1	2	3	4
Formula	C ₈₇ H ₈₂ Ag ₅ Cl ₉ N ₂₀ O ₂₄	C ₈₇ H ₈₂ Ag ₅ Cl ₉ N ₂₀ O ₂₄	C ₉₅ H ₃₈ Ag ₆ Cl ₁₀ F ₁₈ N ₂₀ O ₁₈ S ₆	C ₁₁₀ H ₄₇ Ag ₆ Cl ₄ F ₁₈ N ₂₃ O ₂₄ S ₆
Mol. Wt	2650.12	2650.12	3283.53	3398.08
T (k)	150(2)	293(2)	150(2)	150(2)
System	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	P2 ₁ /n	C2/m	Immm	Immm
a (Å)	22.2116(2)	20.344(1)	17.243(2)	17.2611(1)
b (Å)	17.7686(1)	18.314(9)	17.424(3)	17.4400(1)
c (Å)	27.0088(2)	14.997(8)	20.606(3)	20.5599(2)
α (°)	90	90	90	90
β (°)	109.124(3)	116.719(2)	90	90
γ (°)	90	90	90	90
V (Å ³)	10071.3(1)	4991(4)	6190.9(2)	6189.2(8)
Z	4	2	2	2
D(mg/m ³)	1.748	1.763	1.761	1.823
R ₁ [I > 2σ(I)]	0.1015	0.0801	0.0476	0.0282
wR ² (on F ² , all data)	0.2194	0.1021	0.1644	0.1050

	5	6	7	8
Formula	C ₁₁₃ H ₅₆ Ag ₆ Cl ₄ F ₁₈ N ₂₀ O ₁₈ S ₆	C ₁₁₆ H ₆₂ Ag ₆ Cl ₄ F ₁₈ N ₂₀ O ₁₈ S ₆	C ₁₀₅ H ₄₃ Ag ₆ Cl ₆ N 23O ₂₄	C ₁₁₃ H ₄₇ Ag ₆ Cl ₄ F ₁₈ N ₂₃ O ₁₈ S ₆
Mol. Wt.	3305.15	3347.23	2870.54	3338.11
T (k)	150(2)	150(2)	293(2)	150(2)
System	orthorhombic	orthorhombic	triclinic	orthorhombic
Space group	Immm	Immm	P-1	Immm
a (Å)	17.1390(10)	17.1417(9)	14.168(8)	16.513(3)
b (Å)	17.4670(11)	17.4282(9)	14.209(8)	17.578(5)
c (Å)	20.6218(13)	20.6447(1)	15.139(9)	21.148(5)
α (°)	90	90	65.500(2)	90
β (°)	90	90	85.814(2)	90
γ (°)	90	90	72.974(2)	90
V (Å ³)	6173.5(7)	6167.6(6)	2648(3)	6138(3)
Z	2	2	1	2
D(mg/m ³)	1.778	1.726	1.800	1.729
R ₁ [I > 2σ(I)]	0.0436	0.0438	0.1008	0.0576
wR ² (on F ² , all data)	0.1689	0.0980	0.2376	0.1894

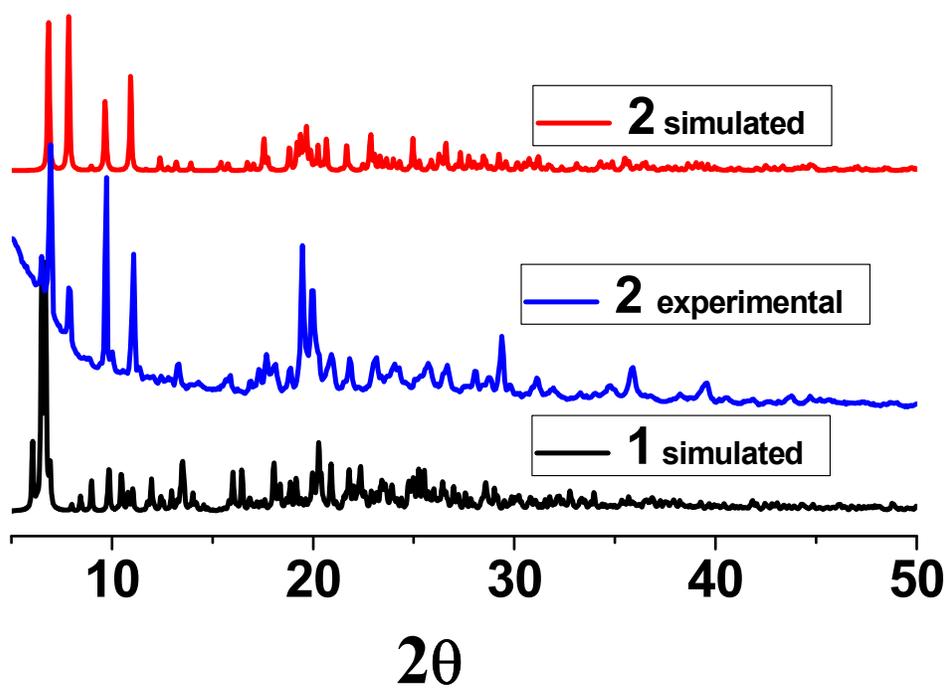


Figure S1. Comparison of PXR D pattern for complex 2.

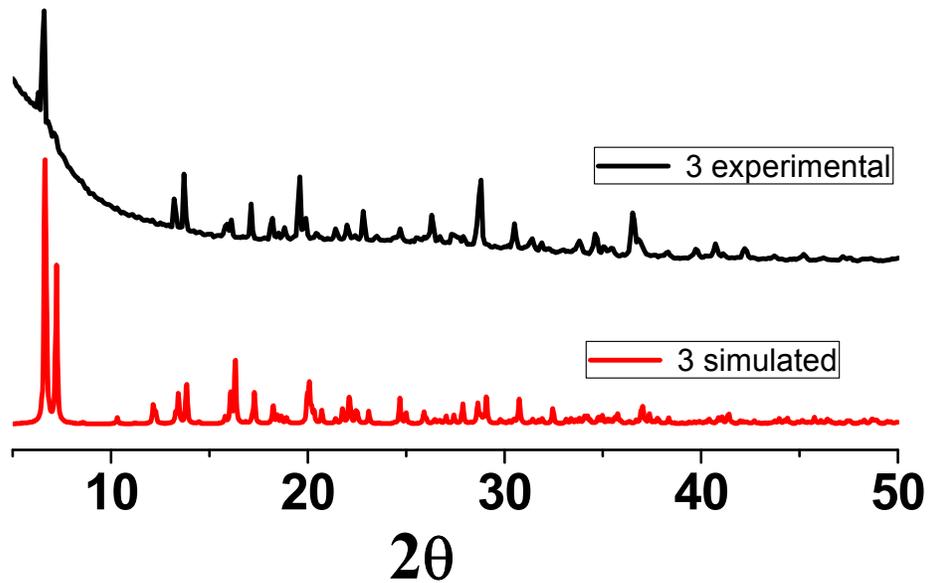


Figure S2. Comparison of PXR D pattern for complex 3.

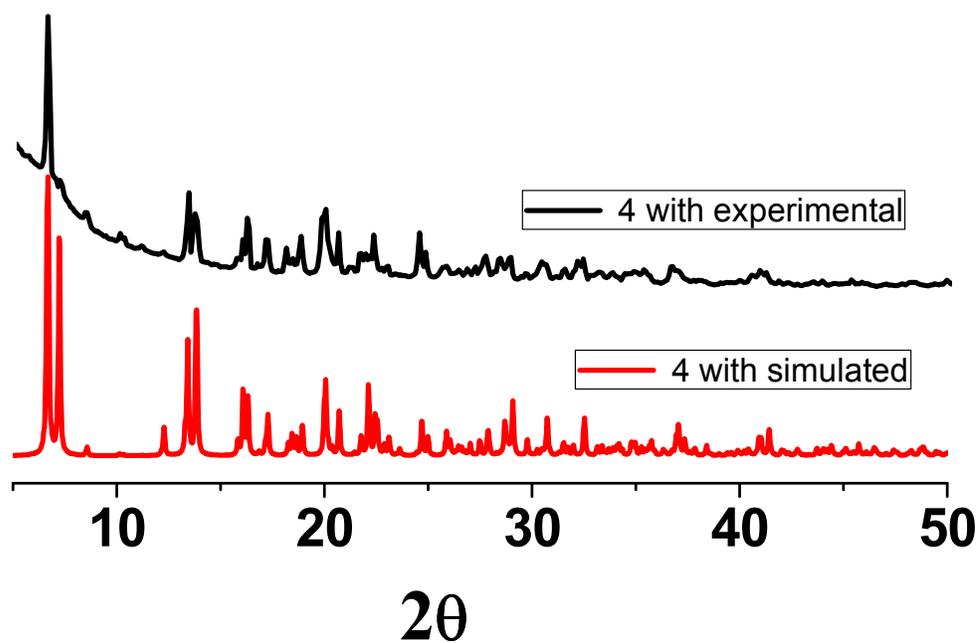


Figure S3. Comparison of PXR D pattern for complex 4.

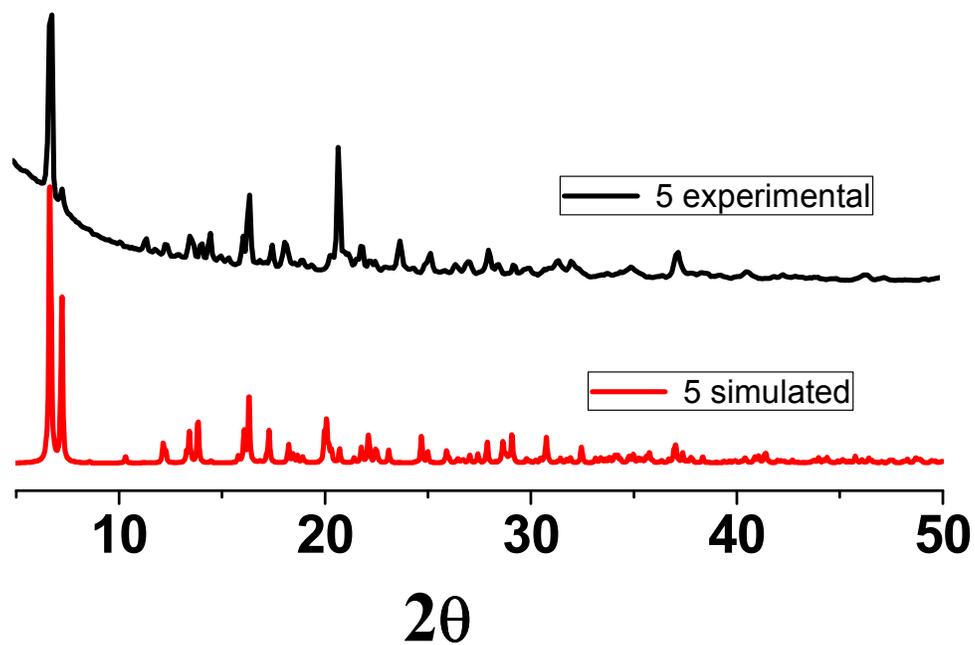


Figure S4. Comparison of PXR D pattern for complex 5.

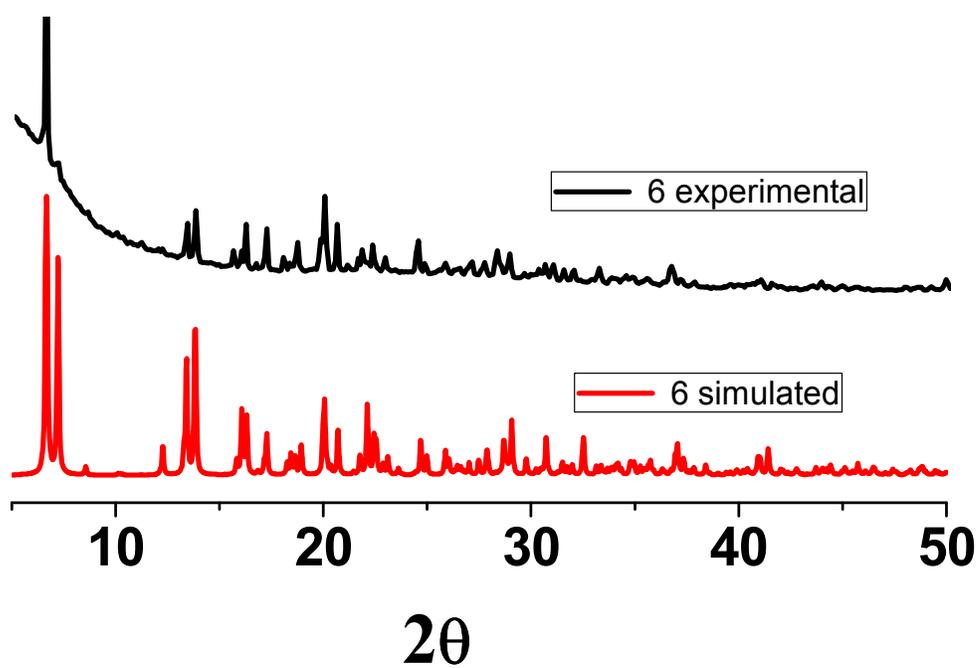


Figure S5. Comparison of PXRd pattern for complex 6.

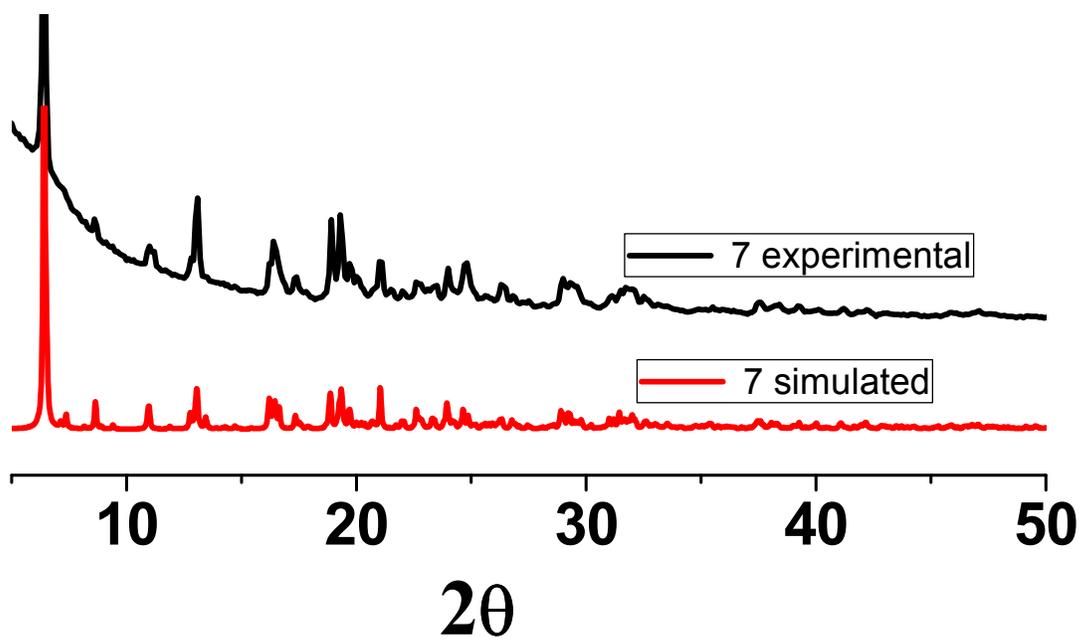


Figure S6. Comparison of PXRd pattern for complex 7.

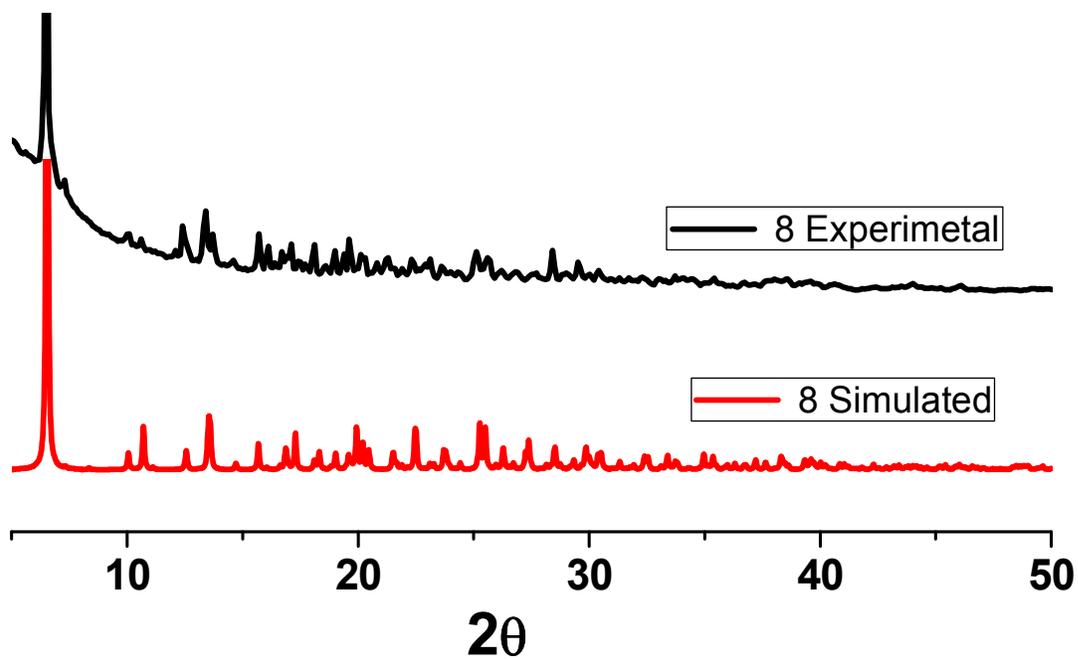


Figure S7. Comparison of PXR D pattern for complex 8.

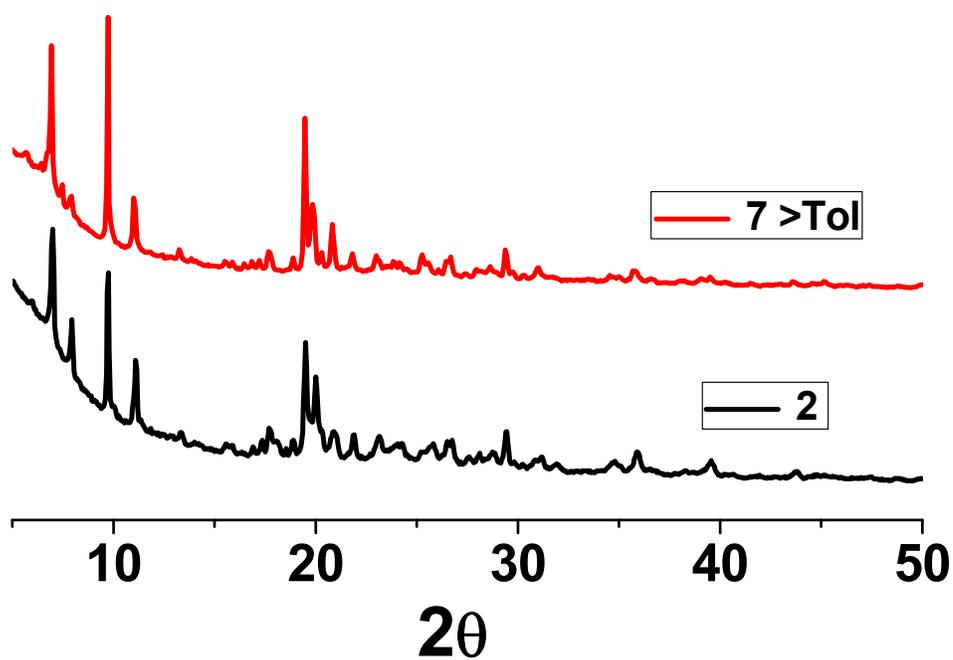


Figure S8. Comparison of PXR D pattern between complex 2 and $[\text{Ag}_6\text{L}_4](\text{ClO}_4)_6 \cdot (3\text{BN})$, 7, by exchanged with toluene

TGA studies:

To check the stability of the framework as well as presence of solvent thermogravimetric analysis (TGA) were carried out at 10°C/ min heating rate. The TGA curve of complex **2** suggest that gradual weight loss of 4.7% up to 100 °C corresponds to the loss of volatile solvent molecules such as 1 unit each of DCM and methanol (expected 2DCM and 1 MeOH solvents) and total 6.3% up to 350 °C corresponds to another three H₂O molecules. The Complex **3** shows gradual weight loss of 10.7% starts from 50 °C up to 350 °C corresponds to the loss of 4.3 units of DCM molecule (expected 5 DCM molecules). The complex **4** exhibits gradual weight loss of 13.5% up to 380 °C corresponds to the loss of 3 units of NB and 1 DCM (expected 3 NB and 2 DCM molecules). The stepwise gradual weight loss of 11% up to 50- 380 °C corresponds to the loss of 2.7 units of Tol and 1.5 units of DCM (expected 3Tol and 2DCM) for complex **5** and 2.7 units of *p*-xy and 1.5 units of DCM (expected 3*p*-xy and 2DCM) for complex **6**. The weight loss of 9.5% at 300- 330 °C for complex **7** and 13.5 % up to 50- 380 °C for complex **8** corresponds to the loss of 2.7 units of BN (expected 3BN) for complex **7** and three units of BN and one unit of DCM (expected 3BN and 2DCM) for complex **8**. The certain discrepancies in the wt% calculation are found due to high volatile nature of DCM, which was present in most of the crystal lattice.

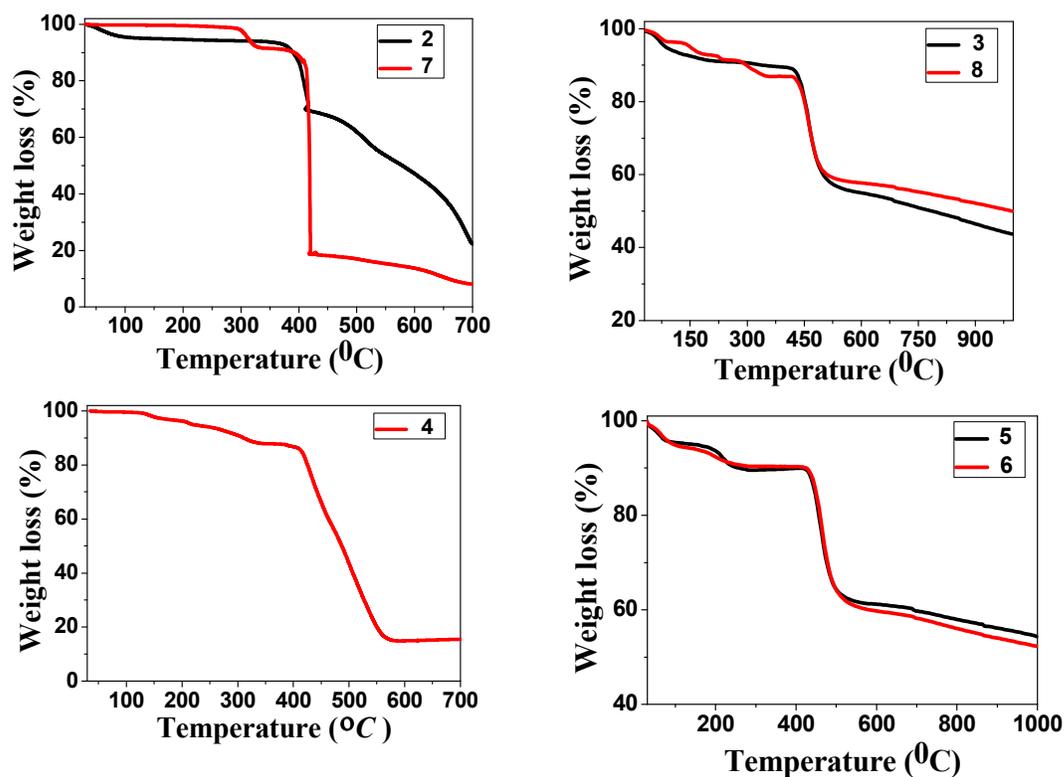


Figure S9. TGA curves for complexes 2-8.

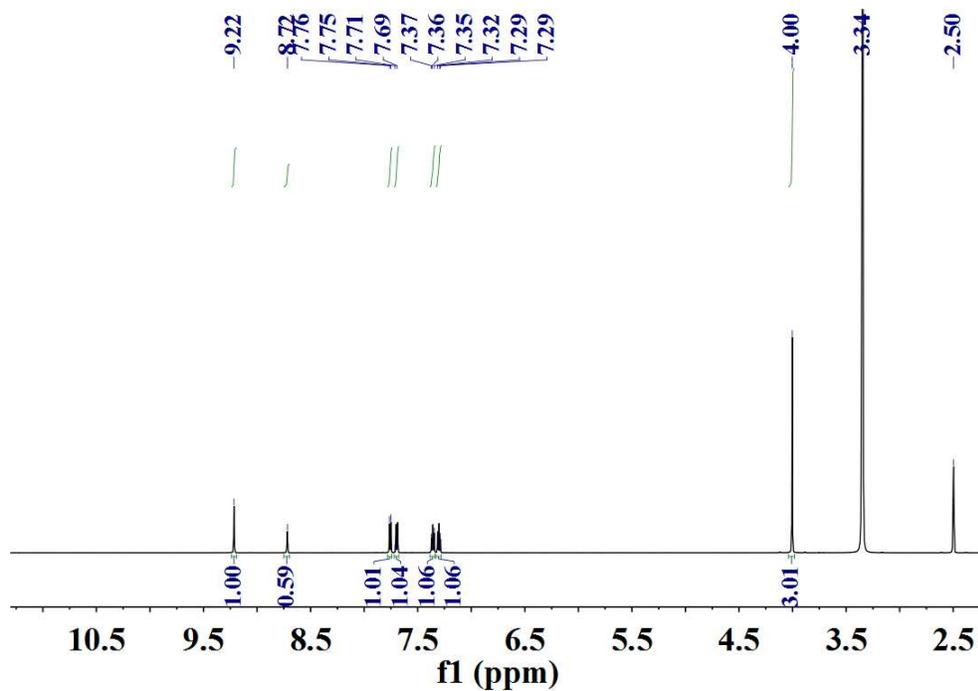


Figure S10. $^1\text{H-NMR}$ of **L** in $\text{D}_6\text{-DMSO}$: δ 9.22 (s, 2H), δ 8.72 (s, 1H), δ 7.76-7.69 (d, 4H), δ 7.38-7.29 (d, 4H), δ 4.0 (s, 6H).

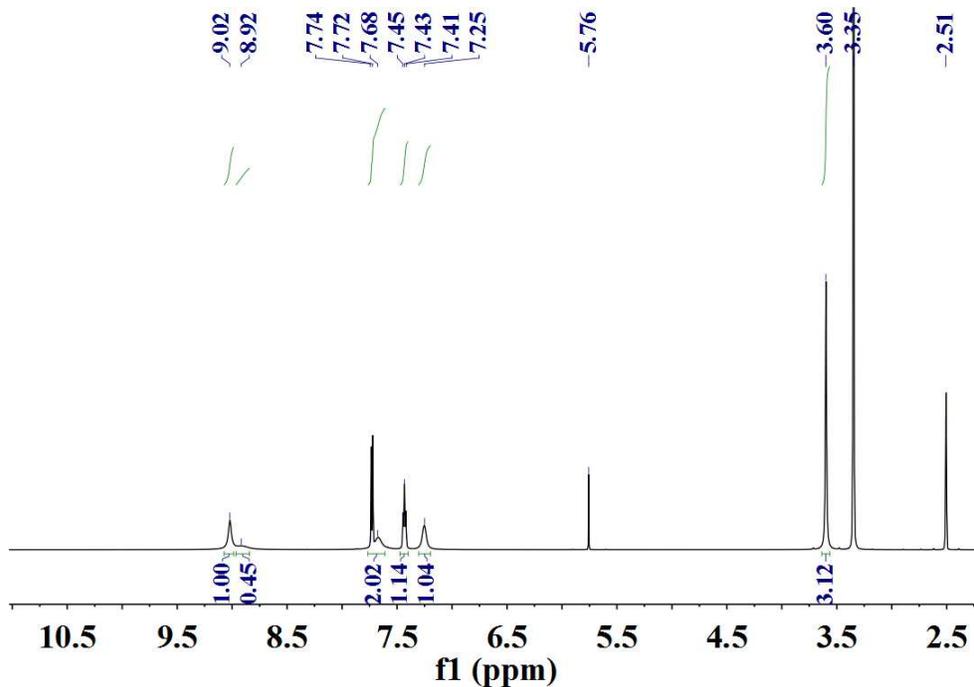


Figure S11. $^1\text{H-NMR}$ of **2** in $\text{D}_6\text{-DMSO}$: δ 9.02 (s, 2H), δ 8.92 (s, 1H), δ 7.74 (d, 4H), δ 7.45 (d, 2H), δ 7.25 (s, 2H), δ 3.60 (s, 6H) for cluster; δ 5.76 (s, for CH_2Cl_2).

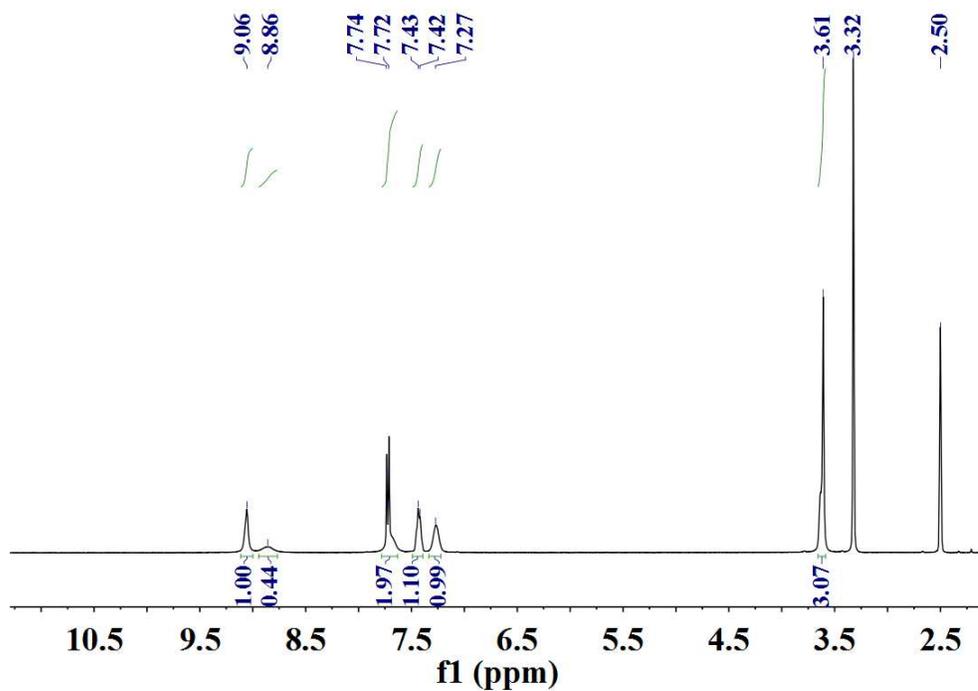


Figure S12. $^1\text{H-NMR}$ of **3** in $\text{D}_6\text{-DMSO}$: δ 9.06 (s, 2H), δ 8.86 (s, 1H), δ 7.74 (d, 4H), δ 7.43 (s, 2H), δ 7.27 (s, 2H), δ 3.61 (s, 6H).

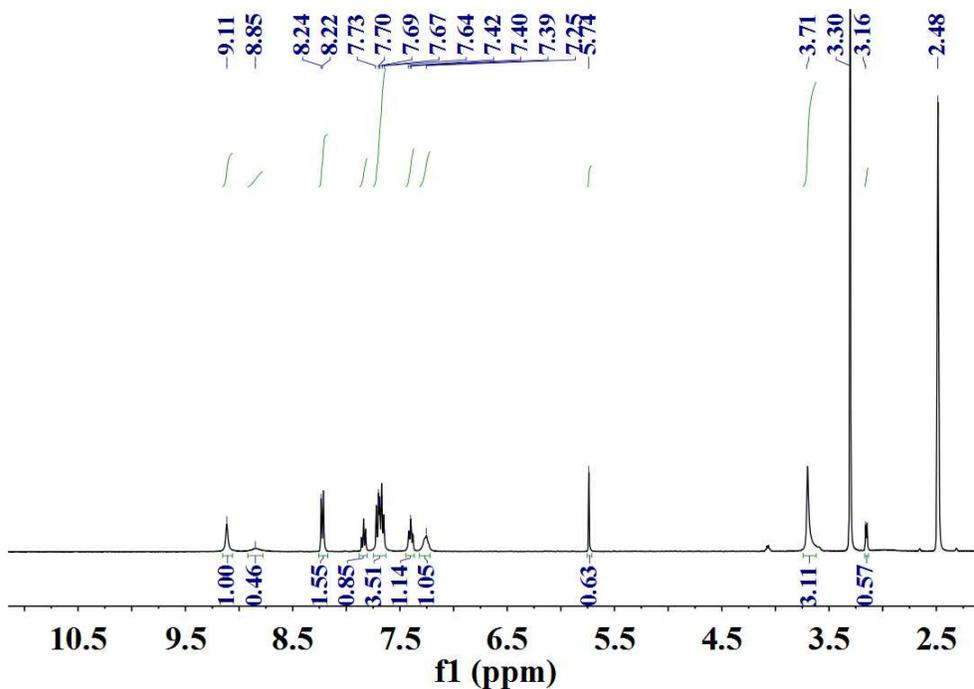


Figure S13. $^1\text{H-NMR}$ of **4** in $\text{D}_6\text{-DMSO}$: δ 9.11 (s, 2H), δ 8.85 (s, 1H), δ 7.73 (m, 6H), δ 7.42 (d, 2H), δ 7.25 (s, 2H), δ 3.71 (s, 6H) for cluster; δ 8.24(d), δ 7.67 (m) for PhNO_2 .

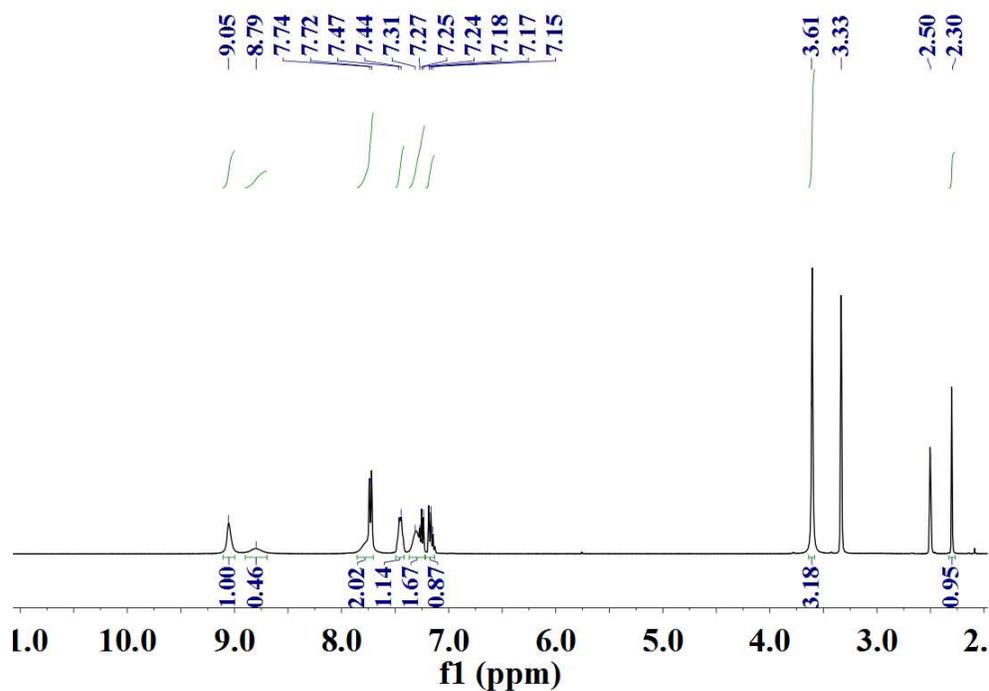


Figure S14. $^1\text{H-NMR}$ of **5** in $\text{D}_6\text{-DMSO}$: δ 9.05 (s, 2H), δ 8.79 (s, 1H), δ 7.74 (d, 4H), δ 7.44 (s, 2H), δ 7.27 (s, 2H), δ 3.61 (s, 6H) for cluster; δ 7.18-7.15 (m), δ 2.30 (s) for toluene.

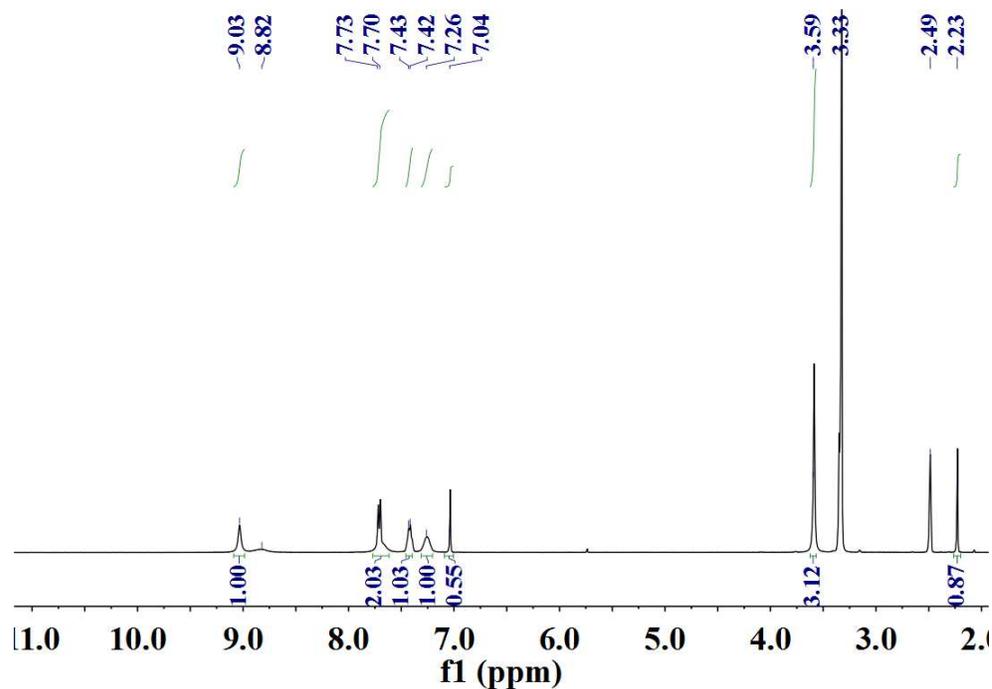


Figure S15. $^1\text{H-NMR}$ of **6** in $\text{D}_6\text{-DMSO}$: δ 9.03 (s, 2H), δ 8.82 (s, 1H), δ 7.73 (d, 4H), δ 7.43 (s, 2H), δ 7.26 (s, 2H), δ 3.59 (s, 6H) for cluster; δ 7.04 (s), δ 2.23 (s) for *p*-xylene.

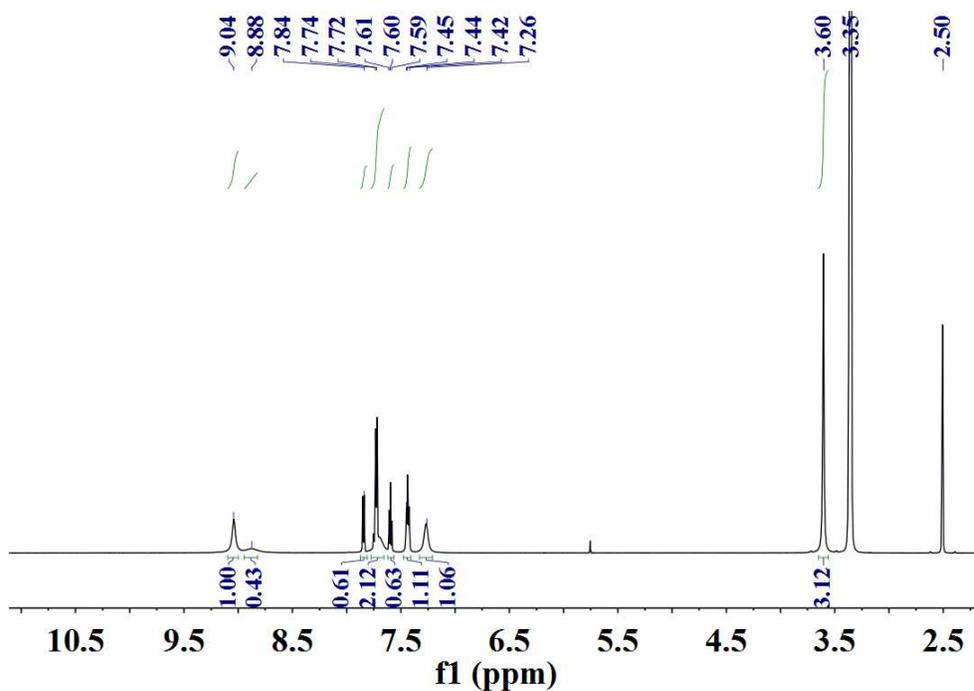


Figure S16. $^1\text{H-NMR}$ of **7** in $\text{D}_6\text{-DMSO}$: δ 9.04 (s, 2H), δ 8.88 (s, 1H), δ 7.74 (d, 4H), δ 7.45 (d, 2H), δ 7.26 (s, 2H), δ 3.60 (s, 6H) for cluster; δ 7.84(d),7.60 (d) for PhCN.

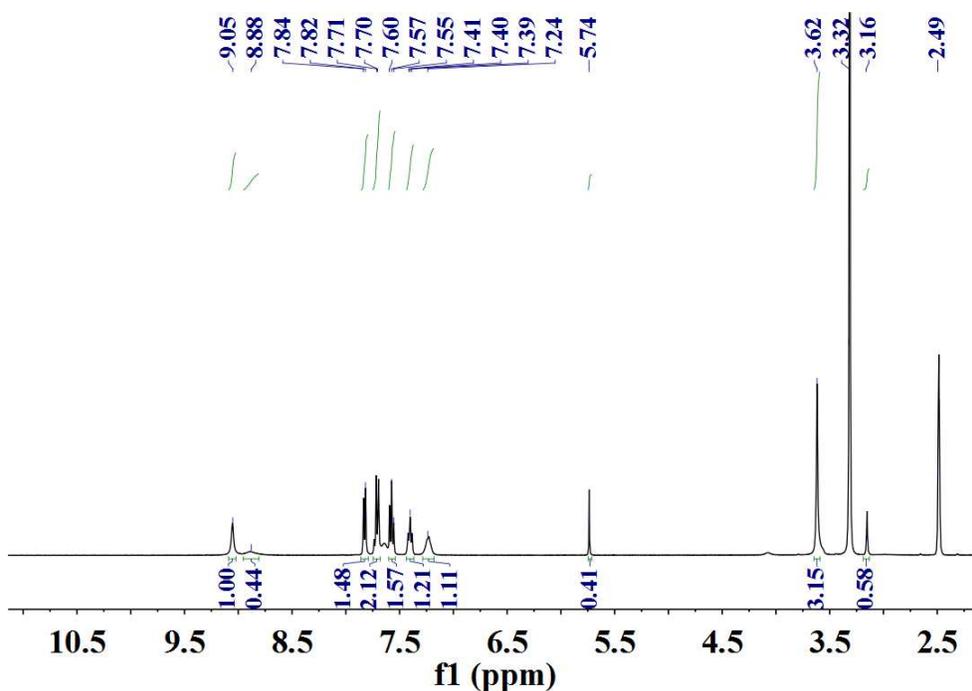


Figure S17. $^1\text{H-NMR}$ of **8** in $\text{D}_6\text{-DMSO}$: δ 9.05 (s, 2H), δ 8.88 (s, 1H), δ 7.71 (d, 4H), δ 7.41 (d, 2H), δ 7.24 (s, 2H), δ 3.62 (s, 6H) for cluster; δ 7.84(d),7.60 (d) for PhCN; δ 5.74(s) for CH_2Cl_2 .

FT-IR studies:

As it was difficult to locate the guest molecule by single crystal structure, so for further characterization we thus tried to monitor by FTIR studies. The IR spectrum of complex **2** and **3** shows no peaks for the benzonitrile or nitrobenzene moiety. In case of **7** and **8**, the appearance of new peak at around 2228 and 2232 cm^{-1} indicates inclusion of benzonitrile molecule as guest in the crystal lattice. Such guest inclusion was also found in complex **4** for nitrobenzene molecule at around 1518 cm^{-1} . In case of toluene and *p*-xylene included complexes **5** and **6**, the resultant peaks are merged with aromatic and aliphatic spacer's frequency.

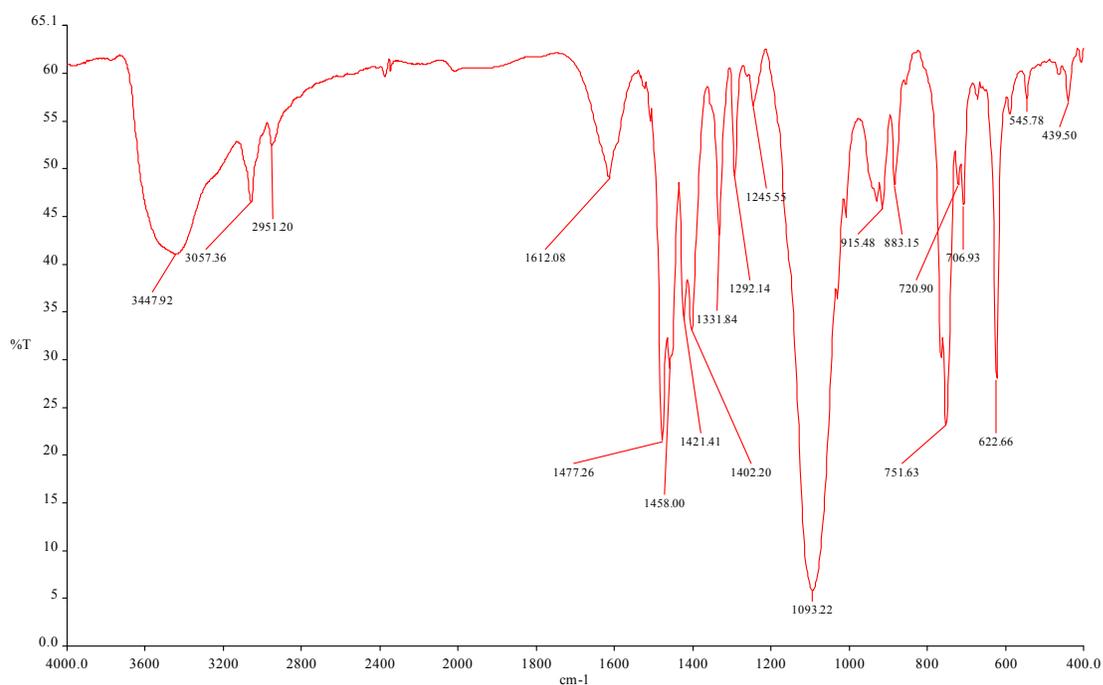


Figure S18. FT-IR spectra for complex-2.

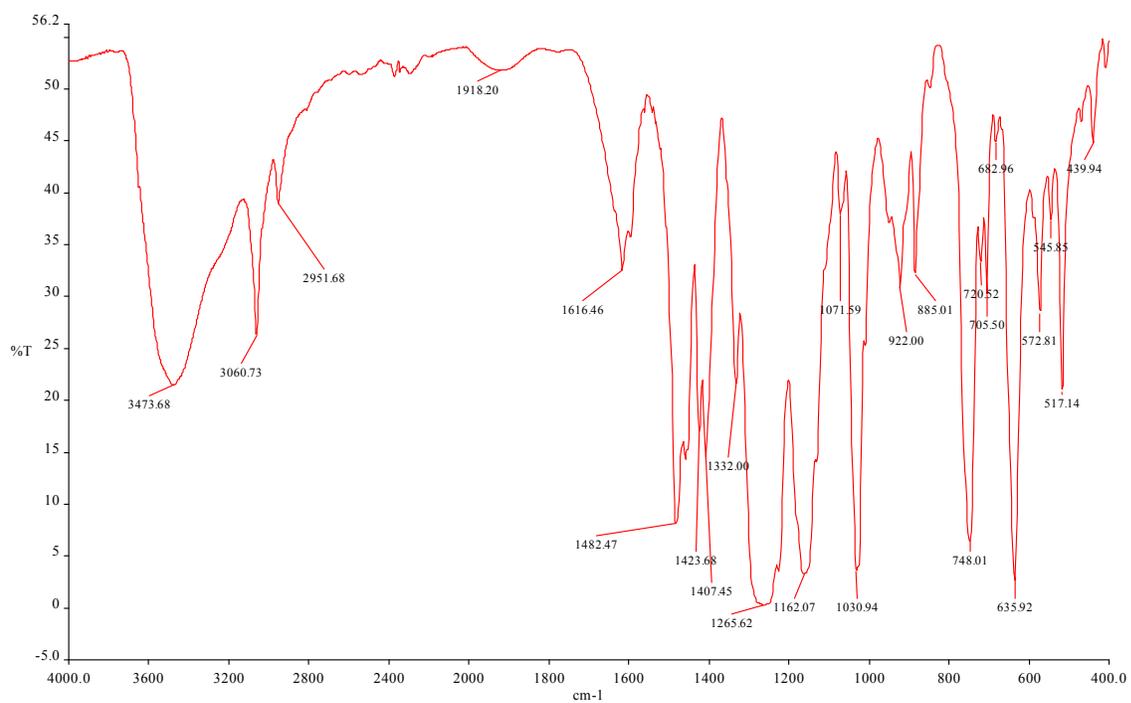


Figure S19. FT-IR spectra for complex-3.

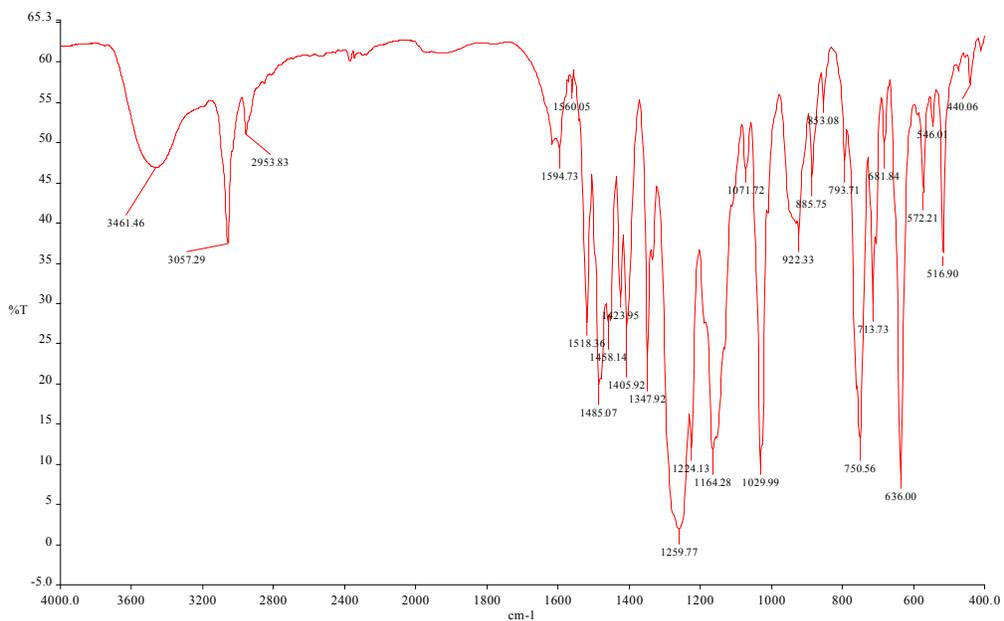


Figure S20. FT-IR spectra for complex-4.

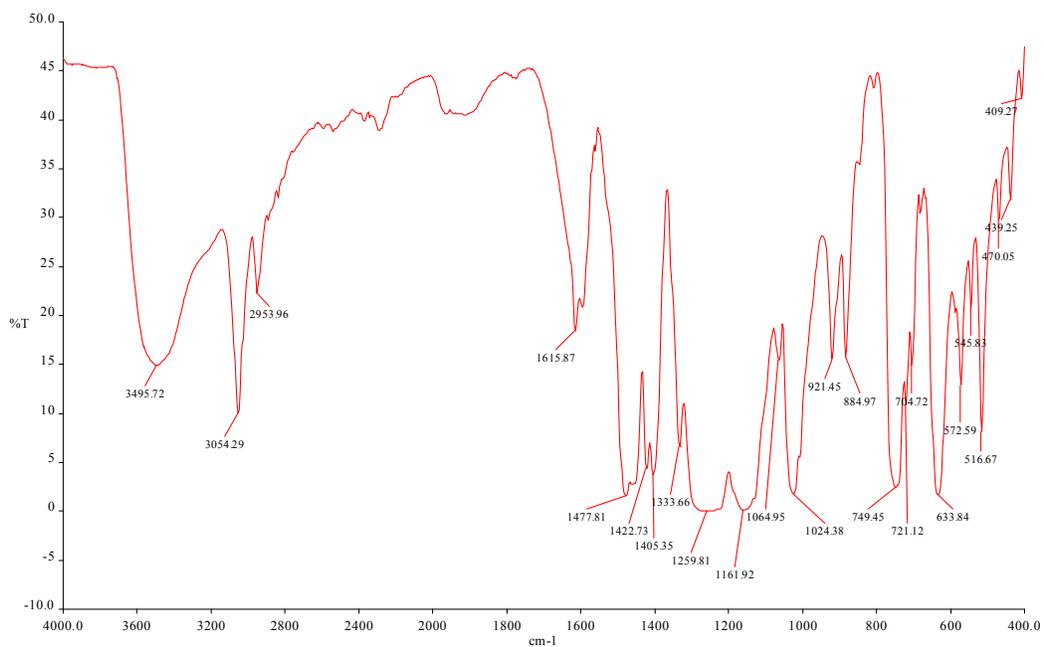


Figure S21. FT-IR spectra for complex-5.

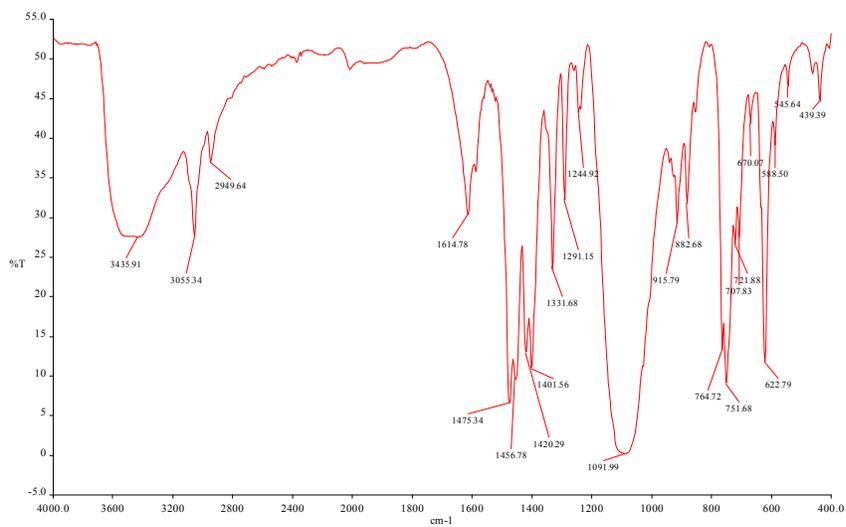


Figure S22. FT-IR spectra for complex-6.

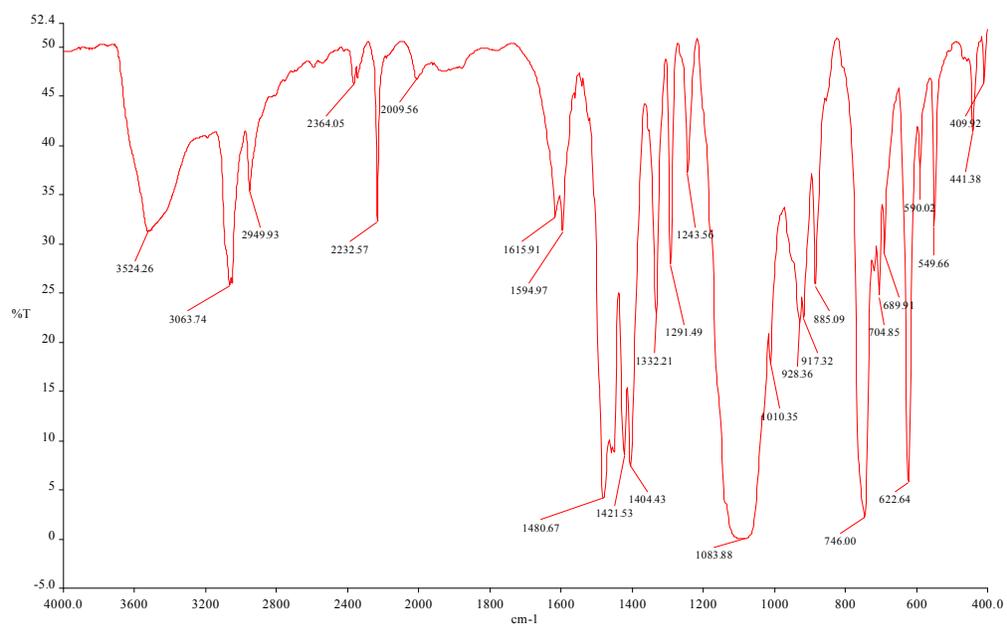


Figure S23. FT-IR spectra for complex-7.

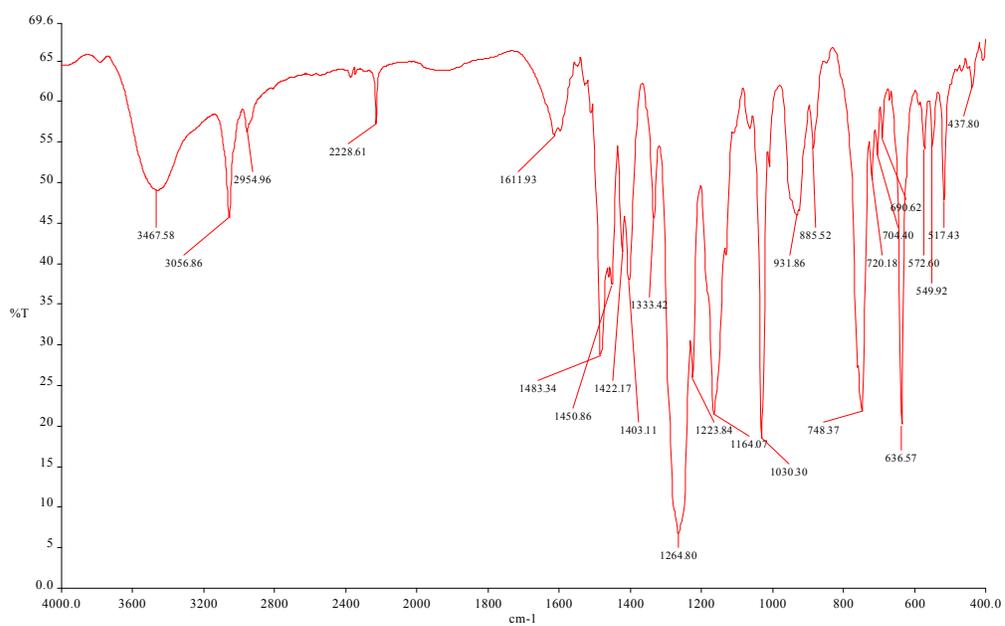


Figure S24. FT-IR spectra for complex-8.

Luminescence curves:

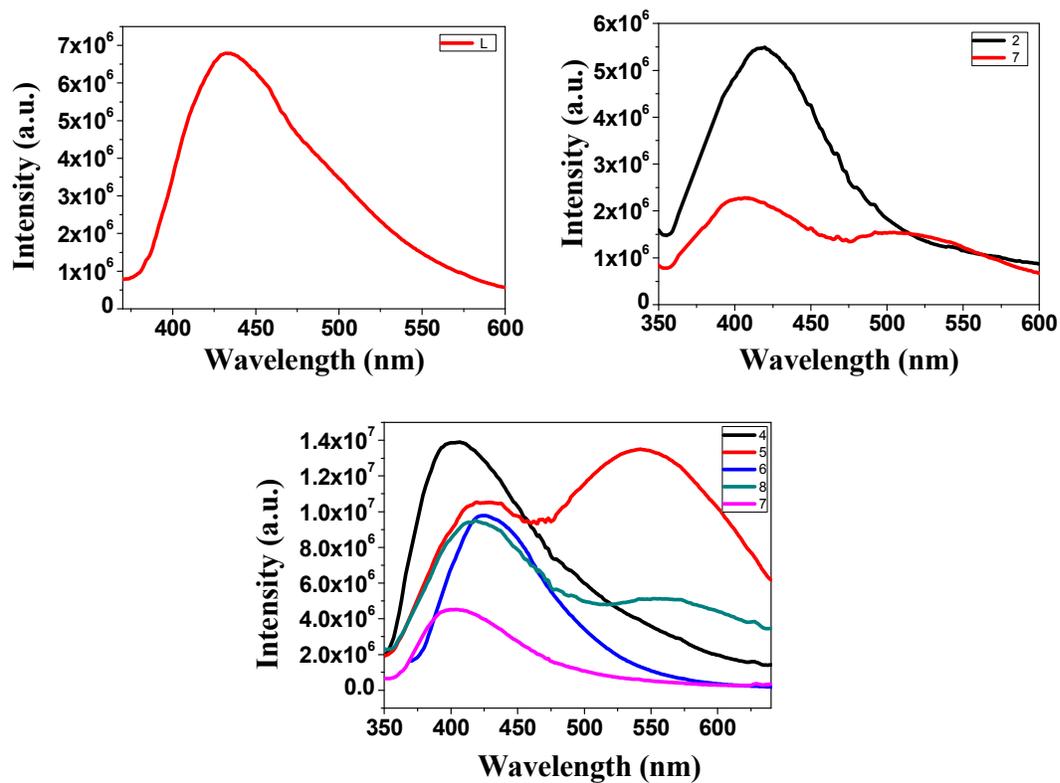


Figure S25. Solid state fluorescence spectra for complexes 2-8.

Guest characterization by GCMS:

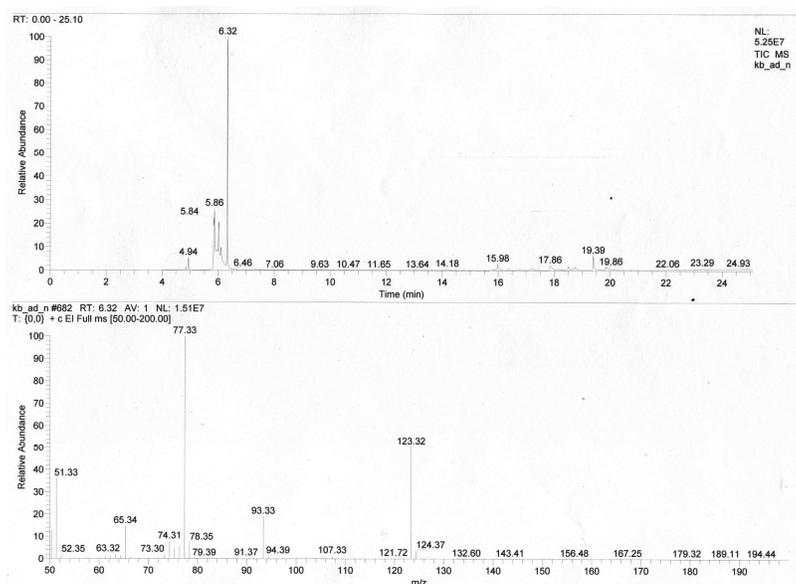


Figure S26. GCMS for complex 4 where m/z at 123.32 corresponds to nitrobenzene.

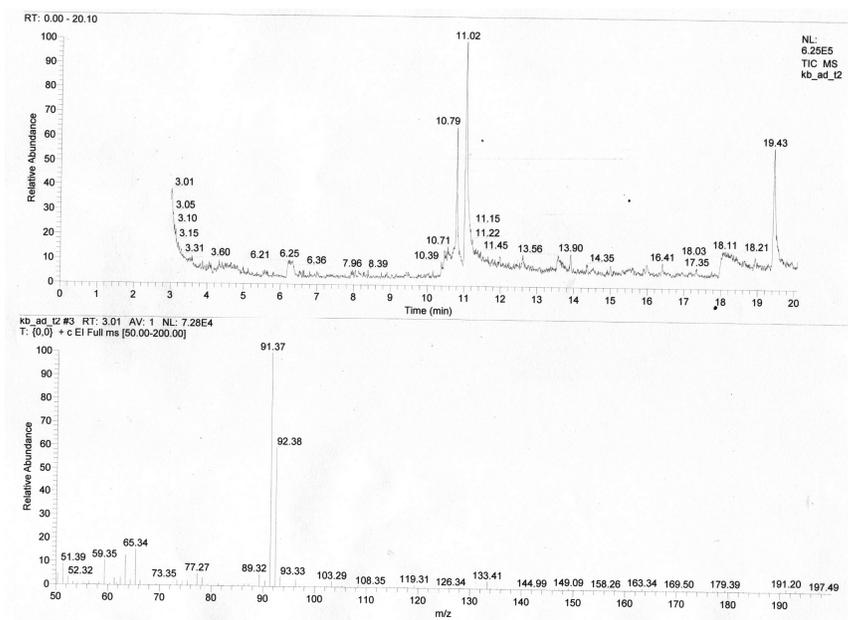


Figure S27. GCMS for complex 5 where m/z at 92.38 corresponds to toluene.

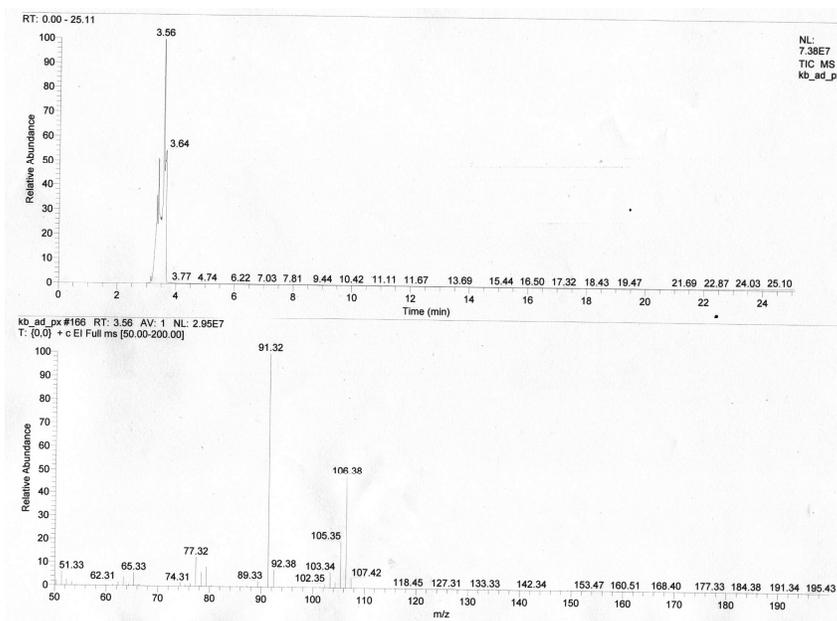


Figure S28. GCMS for complex 6 where m/z at 106.38 corresponds to *p*-xylene.

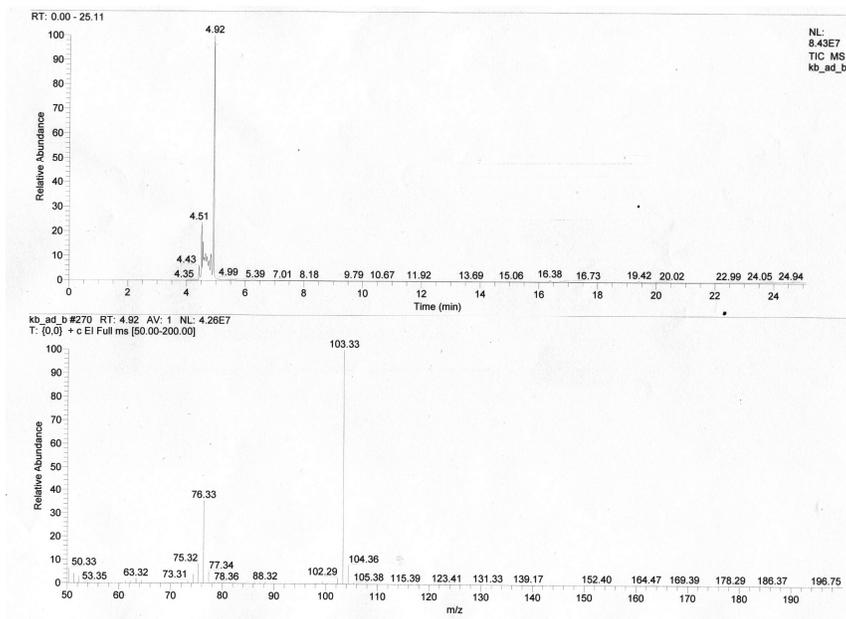
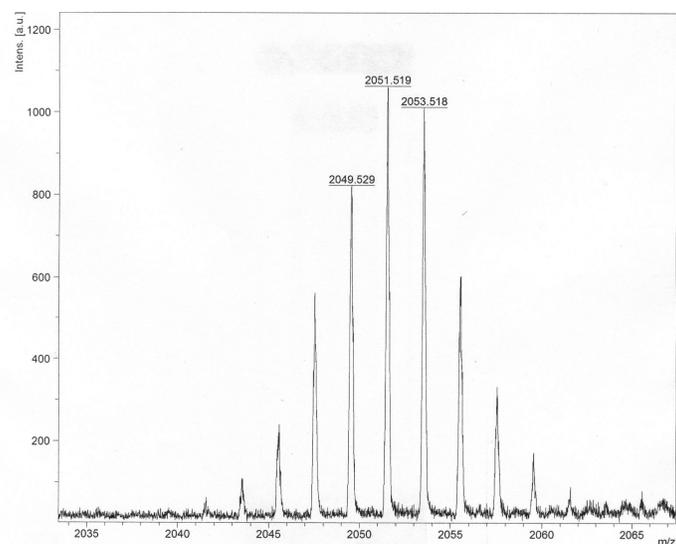
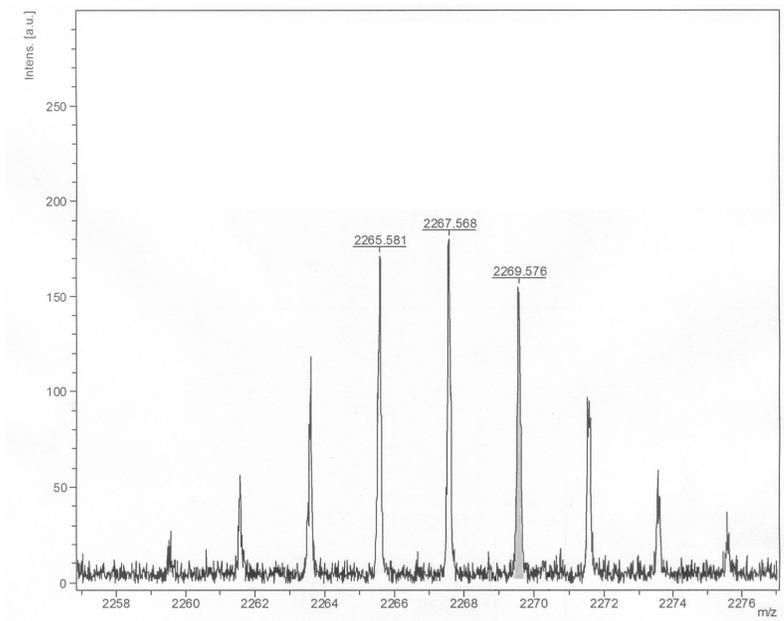


Figure S29. GCMS for complex **8** where m/z at 103.33 corresponds to benzonitrile.

MALDI-TOF analysis:

The MALDI-TOF mass spectra analysis was carried out 2,5-dihydroxy benzoic acid as matrix. The presence of maximum molecular ion peak at > 2000 clearly indicates structural integrity of the clusters in solution. The molecular ion peak at 2051 corresponds to the Ag_5L_4 cluster; whereas 2267 corresponds to the Ag_6L_4 cluster.





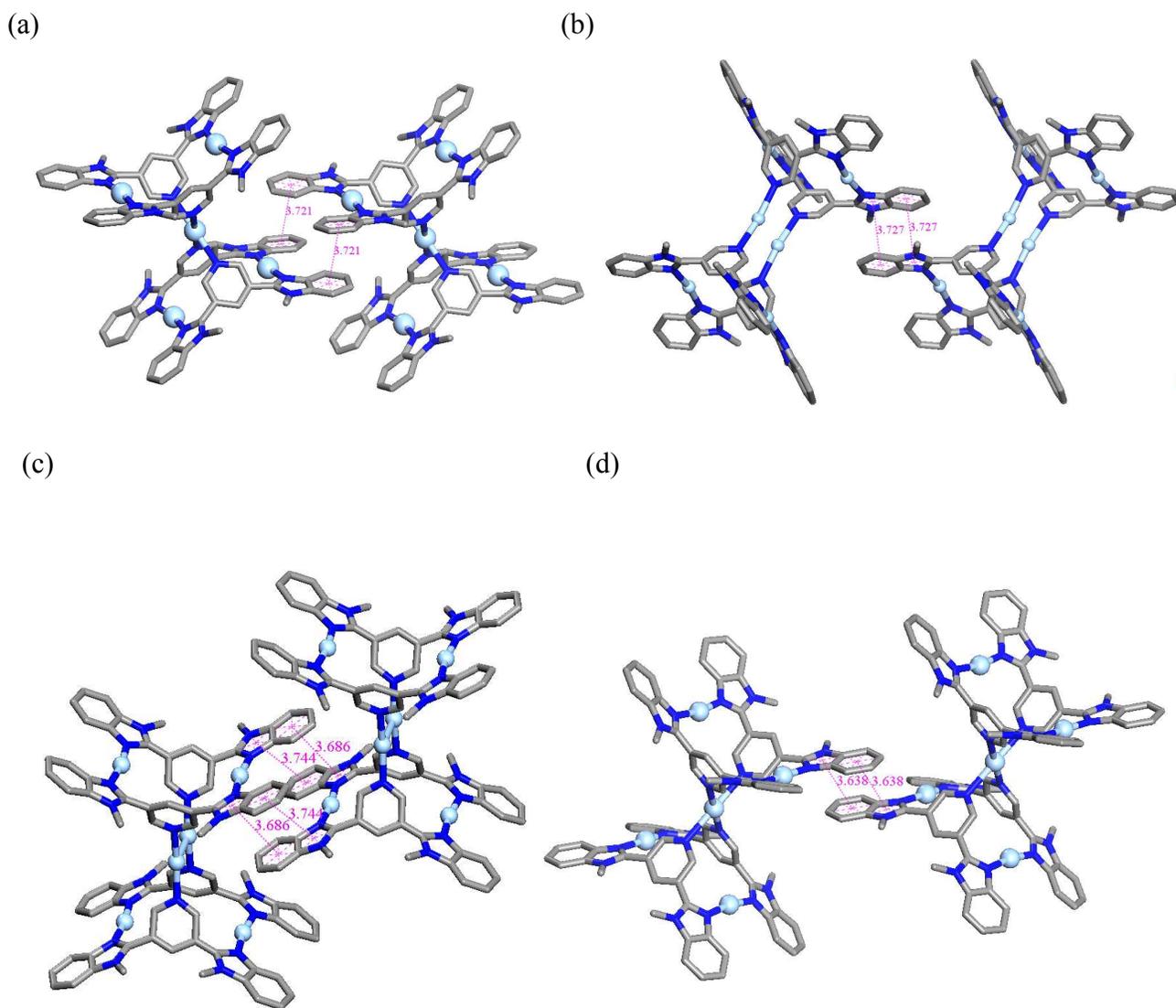
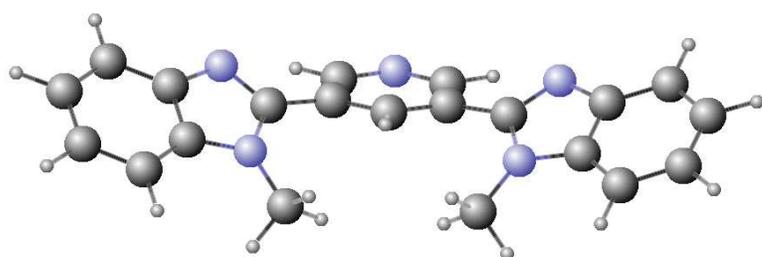


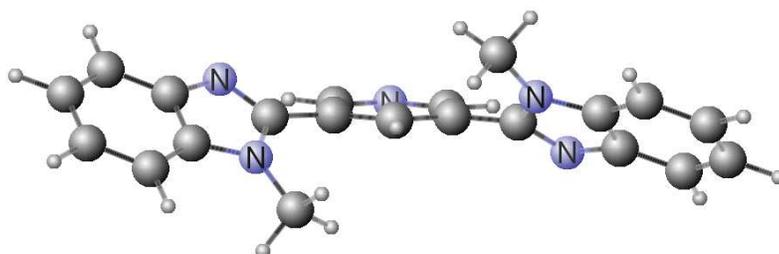
Figure S30. π - π stacking for complexes **2**(a), **3**(b), **7**(c) and **8**(d).

S31. Relative energy calculation for conformational stability

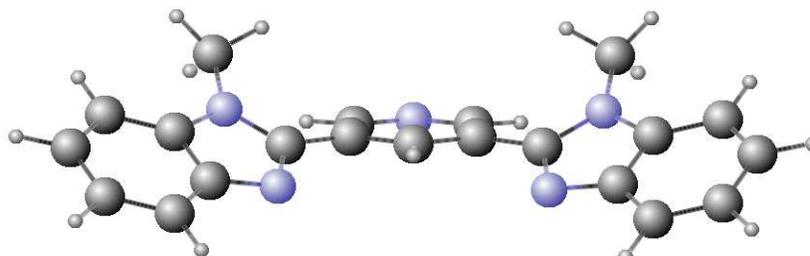
We have considered six different conformations for the arc shape tridented molecule. They are generated by C-C single bond rotation on either side of the pyridine ring. The relative energies (in kcal/mol) of these conformations are given below in table. Symbol α and β represents angle between the each group of bim moieties with the plane of the pyridine ring.



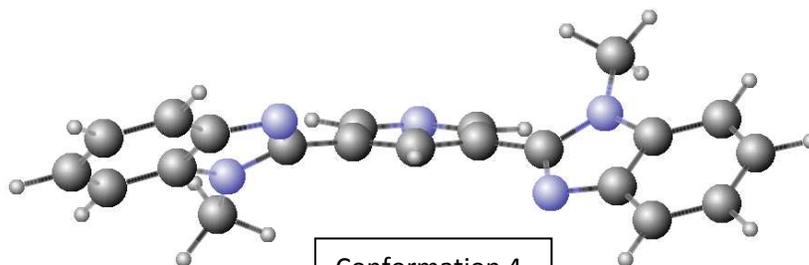
Conformation 1



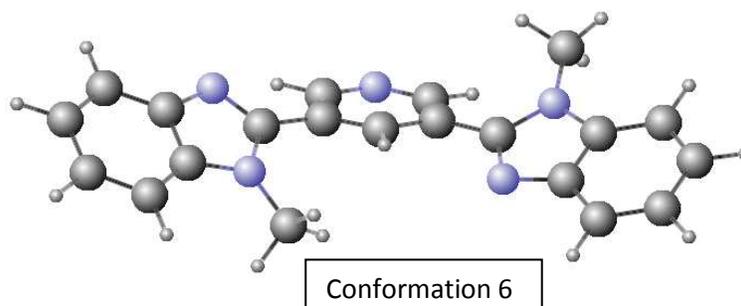
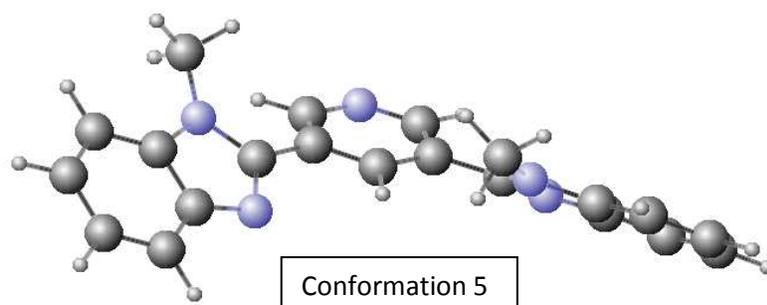
Conformation 2



Conformation 3



Conformation 4



Model	Relative Energy (kcal/mol)	α (degree)	β (degree)
Conformation 1	2.01	31	33
Conformation 2	1.72	35	-36
Conformation 3	1.49	143	144
Conformation 4	0.93	141	-141
Conformation 5	0.64	146	30
Conformation 6	0.00	145	-32

Geometry optimizations of all these models were performed at the hybrid density functional B3LYP³ level of theory with resolution of the identity (RI⁴) approximation. The basis set def2-SVP⁵ and the corresponding auxiliary basis set was used for all calculations. We used empirical dispersion correction (DFT-D3)⁶. All the calculations were done with TURBOMOLE⁷⁻⁸ software.

References:

1. Sheldrick, G.M. *SHELXL*- 2014; University of Göttingen and Bruker AXS, Karlsruhe, Germany, 2014.
2. Spek, A. L. *PLATON: A Multi Purpose Crystallographic Tool*; Utrecht University, Utrecht, the Netherlands, 2002.
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