

Cooperative Effect of "Flexible" Interaction and "Flexible" Framework in Reversible Intake and Removal of Aromatic Guest Molecules

Kumari Suman,^a Rajnikant,^b Vivek K. Gupta^b and Madhushree Sarkar*^a

^a Department of Chemistry, Birla Institute of Technology and Science , Pilani, Pilani Campus, Rajasthan, India. Fax: +91-1596-244183; Tel: +91-1596-245073; E-mail: msarkar@pilani.bits-pilani.ac.in

^b Post Graduate Department of Physics, University of Jammu, Jammu Tawi, India. Fax/Tel:+91-191-2432051 E-mail: rkvk.paper11@gmail.com

Supporting Information

(Synthesis details, ORTEP, IR Spectra, Powder XRD, Solid State UV-Vis)

General: Infra-red spectrum was recorded in FTIR ABB Bomen MB-3000. UV-Vis absorption spectra were recorded in Shimadzu Spectrophotometer with model UV-2450. Elemental analyses were obtained with a Thermo finnigan, Italy, Model FLASH EA 1112 series. Thermogravimetric analysis (TGA) data were recorded under a N₂ atmosphere at a heating rate of 2°Cmin⁻¹ with a Perkin-Elmer instrument. Powder X-ray diffraction (XRD) data were recorded with a Rigaku miniflex II, $\lambda = 1.54$, Cu K α . DSC was performed by DSC-60 Shimadzu, Pan-Copper, N₂ atmosphere, Heating rate: 10°C/minute. The single crystal data was collected on a Xcalibur, Sapphire3 X-ray diffractometer that uses graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by the ω -scan method.¹ The structures were solved by direct methods and refined by least square methods on F² using SHELX-97.² Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.

Synthesis of Ligand: The ligand was synthesized according to a literature procedure². 3-Amino pyridine (2 mmol) was added to 40 mL of a pyridine solution of succinic acid (1 mmol), and the solution was stirred for 15 min. To this solution was added triphenyl phosphite (2 mmol), and the mixture was refluxed for 5 h. The volume of the solution was reduced to 5 mL by distilling out the pyridine, and a white precipitate was obtained. The solid was filtered, washed with water, and dried under vacuum. Yield: 70 %. Mp: 195–198°C; IR (cm⁻¹): 3301(w), 3232(m), 3178(m), 3116(m), 3039(s), 2954(vs), 2908(vs), 1689(vs), 1612 (s), 1589(vs), 1550(vs), 1473(s), 1419(vs), 1326(vs), 1272(s), 1157(vs), 1126(m), 1033(m), 948 (w), 856 (s), 802(s), 694(s), 617 (m).

Synthesis of crystals of 3: A solution of NH₄PF₆ (65.2 mg, 0.4 mmol) in 2mL water was added to a stirred solution of the ligand (54 mg, 0.2 mmol) in 5 mL of (1:1) water-ethanol solution. An ethanolic solution (2 mL) of Cu(NO₃)₂ (25 mg, 0.1 mmol) was layered over the ligand solution. This resulted in the formation of a blue precipitate. Blue colored crystals were formed after 1 week in 70 % yield. Elemental Analysis: C₂₈H₃₂CuF₁₂N₈O₆P₂ (930.08) Calculated: C 36.16 % , H 3.47 % ; Found: C 35.3854 % , H 3.4610 % ; IR (cm⁻¹): 3386(s), 3280(m), 3185(w), 3109(w), 3073(w), 3054(w), 1688(vs), 1612(m), 1535(vs), 1488(s), 1419(m), 1334(m), 1288(m), 1195(m), 1149(w), 1110(w), 1064(w), 972(w), 826(vs), 702(m), 617(m), 547(s)

The above reaction was also performed by taking aromatic solvents. A solution of NH₄PF₆ (65.2 mg, 0.4 mmol) in 2mL water was added to a stirred solution of the ligand (54 mg, 0.2 mmol) in 5 mL of (1:1) water-ethanol solution. To this solution, 5mL of

nitrobenzene/benzonitrile/toluene/xylenes were added and the solution was stirred for 30 min. An ethanolic solution (2 mL) of $\text{Cu}(\text{NO}_3)_2$ (25 mg, 0.1 mmol) was layered over the ligand solution. Blue colored crystals were formed after 10 days.

Synthesis of Complex 4a-c by anion exchange reaction: The anion exchange reactions were performed by immersing the crystals of complex **3** (0.05 mmol) in ethanol solution (5mL) of NaClO_4 (0.2mmol). To this, 5mL of nitrobenzene/benzonitrile/*p*-xylenes was added. After three days, the crystals were characterized by IR and powder XRD.

IR (cm^{-1}) 4a: 3325(s), 3101(w), 3070(w), 1681(s), 1612(m), 1527(vs), 1488(s), 1411(m), 1334(vs), 1288(m), 1195(w), 1065(s), 972(w), 810(w), 702(w), 617(s), 555(m)

4b: 3409(w), 3325(m), 3070 (m), 2229 (s), 1689 (s), 1604(w), 1542(s), 1488(s), 1450(m), 1411(w), 1334(w), 1288(m), 1249(w), 1064(s), 756(vs), 686(vs)

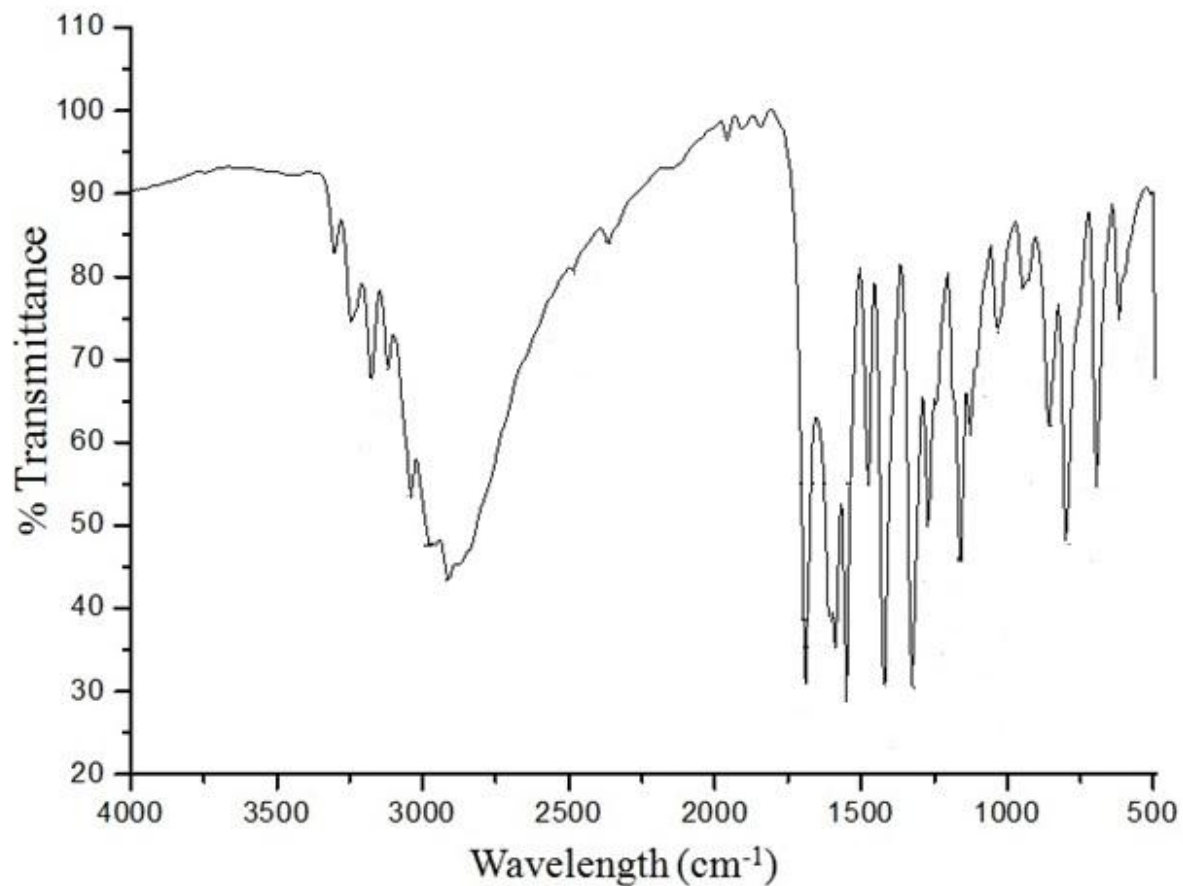
4c: 3325(s), 3101 (w), 1689 (s), 1612(w), 1544(vs), 1488(s), 1411(m), 1334(m), 1288(m), 1248(w), 1195(w), 1064(vs), 972(w), 925(w), 810(m), 702(s), 617(s)

Preparation of Apohost 4: 4a/4b/4c/4d was washed thoroughly with CHCl_3 and then keeping under vacuum for 4-5h.

IR (cm^{-1}): 3325(m), 3101 (w), 3070(w), 1681 (vs), 1612(m), 1542(vs), 1488(s), 1411(m), 1334(m), 1288(m), 1195(m), 1064(vs), 972(w), 925(w), 810(m), 702(s), 617(s)

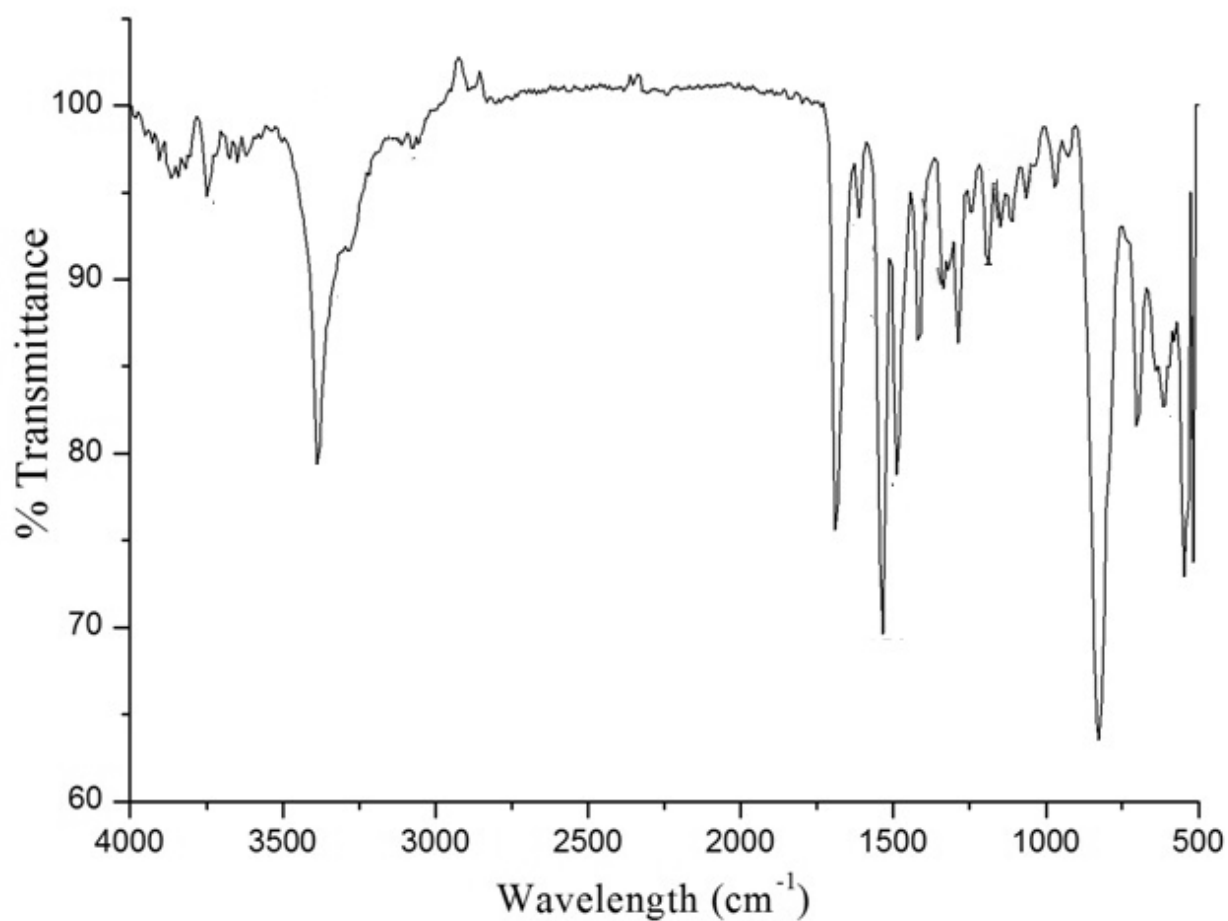
Anion exchange reaction of 4a-c with NH_4PF_6 : The anion exchange reactions were performed by immersing the crystals of complex **4a/b/c** (0.05 mmol) in ethanol solution (5mL) of NH_4PF_6 (0.2mmol). To this, 5mL of nitrobenzene/benzonitrile/*p*-xylene was added. After three days, the crystals were characterized by IR and powder XRD.

Figure S1: IR spectra of Ligand 1a:



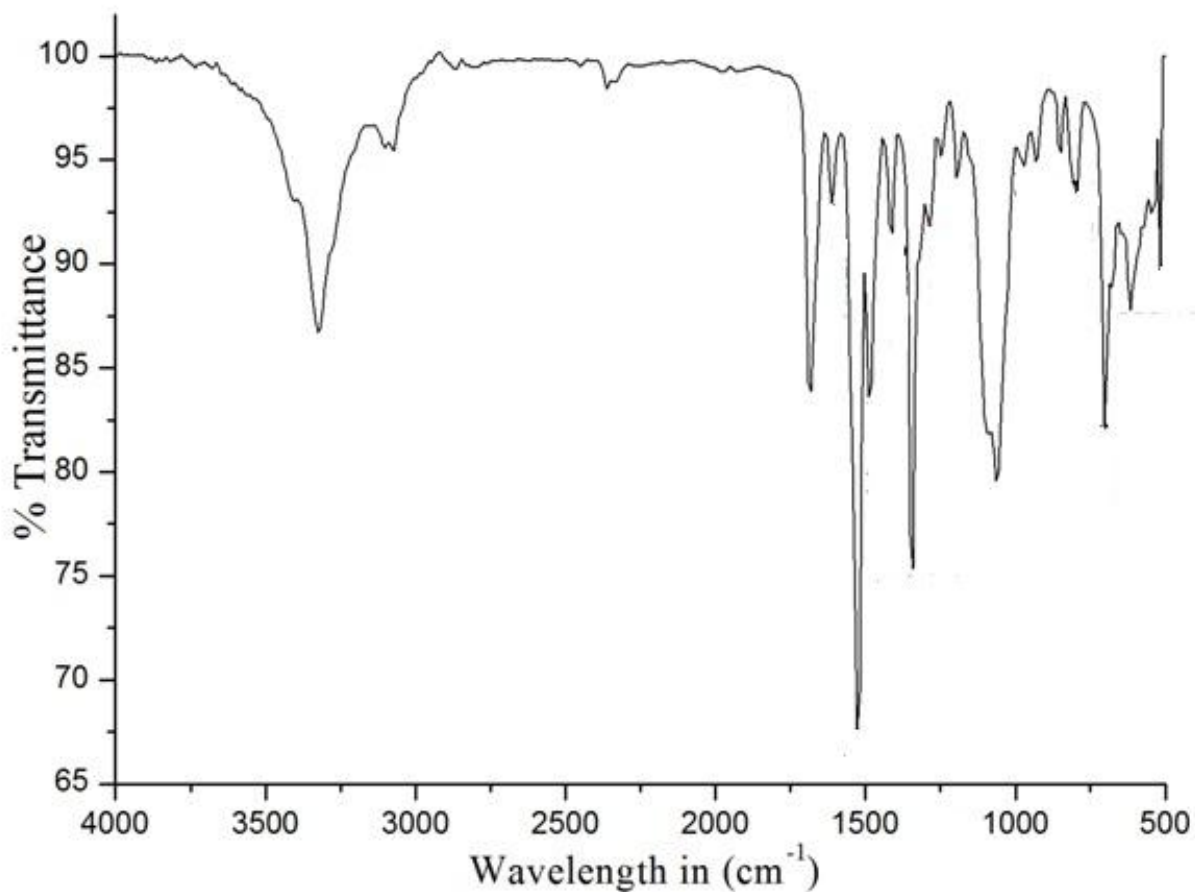
IR (cm⁻¹): 3301(w), 3232(m), 3178(m), 3116(m), 3039(s), 2954(vs), 2908(vs), 1689(vs), 1612 (s), 1589(vs), 1550(vs), 1473(s), 1419(vs), 1326(vs), 1272(s), 1157(vs), 1126(m), 1033(m), 948 (w), 856 (s), 802(s), 694(s), 617 (m)

Figure S 2: IR spectra of complex 3:



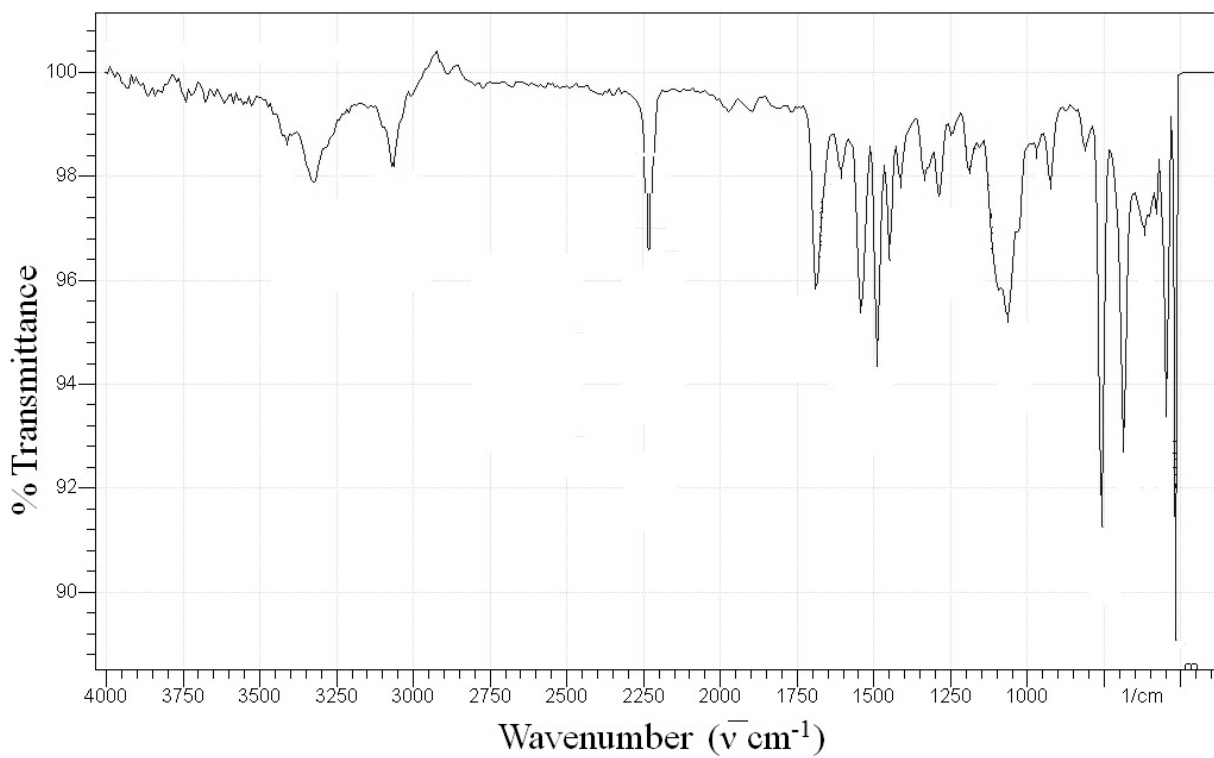
IR (cm⁻¹): 3386(s), 3280(m), 3185(w), 3109(w), 3073(w), 3054(w), 1688(vs), 1612(m), 1535(vs), 1488(s), 1419(m), 1334(m), 1288(m), 1195(m), 1149(w), 1110(w), 1064(w), 972(w), 826(vs), 702(m), 617(m), 547(s)

Figure S 3. IR spectra of complex 4a:



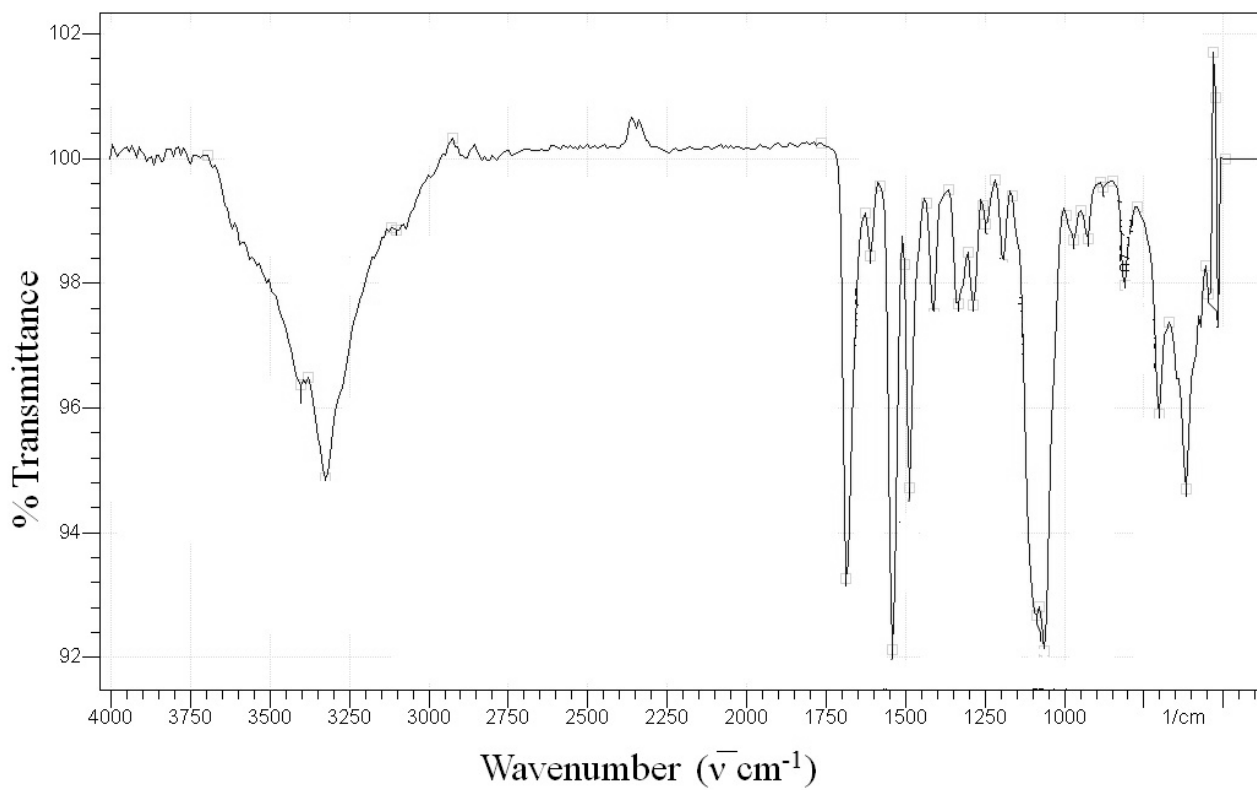
IR (cm⁻¹): 3325(s), 3101(w), 3070(w), 1681(s), 1612(m), 1527(vs), 1488(s), 1411(m), 1334(vs), 1288(m), 1195(w), 1065(s), 972(w), 810(w), 702(w), 617(s), 555(m)

Figure S 4. IR spectra of complex 4b:



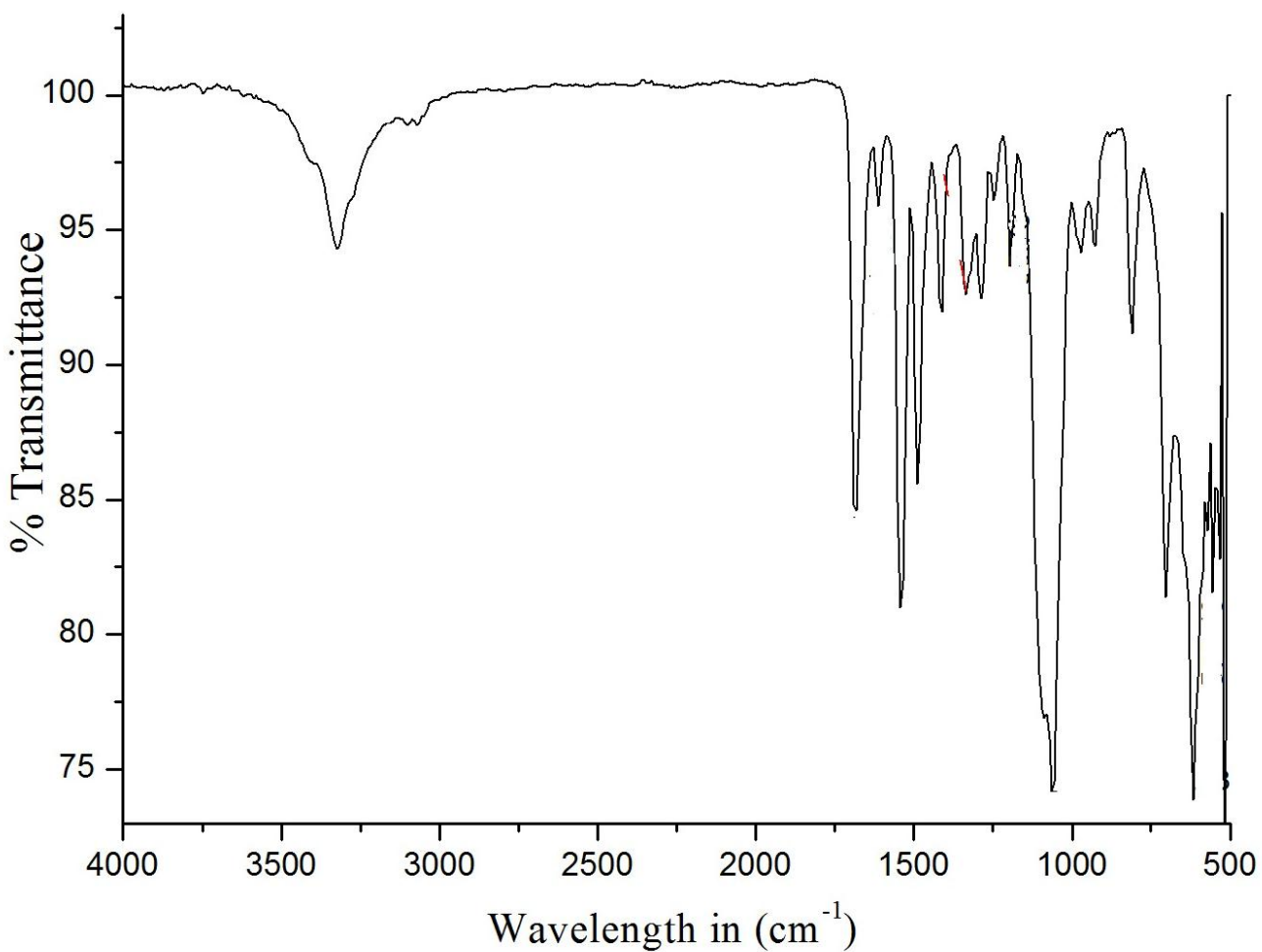
IR (cm^{-1}): 3409(w), 3325(m), 3070 (m), 2229 (s), 1689 (s), 1604(w), 1542(s), 1488(s), 1450(m), 1411(w), 1334(w), 1288(m), 1249(w), 1064(s), 756(vs), 686(vs)

Figure S 5. IR spectra of complex 4c:



IR (cm⁻¹): 3325(s), 3101 (w), 1689 (s), 1612(w), 1544(vs), 1488(s), 1411(m), 1334(m), 1288(m), 1248(w), 1195(w), 1064(vs), 972(w), 925(w), 810(m), 702(s), 617(s)

Figure S 6. IR Spectra of Apohost 4:



IR (cm⁻¹): 3325(m), 3101 (w), 3070(w), 1681 (vs), 1612(m), 1542(vs), 1488(s), 1411(m), 1334(m), 1288(m), 1195(m), 1064(vs), 972(w), 925(w), 810(m), 702(s), 617(s)

Figure S 7. Powder XRD of 3 (Experimental)

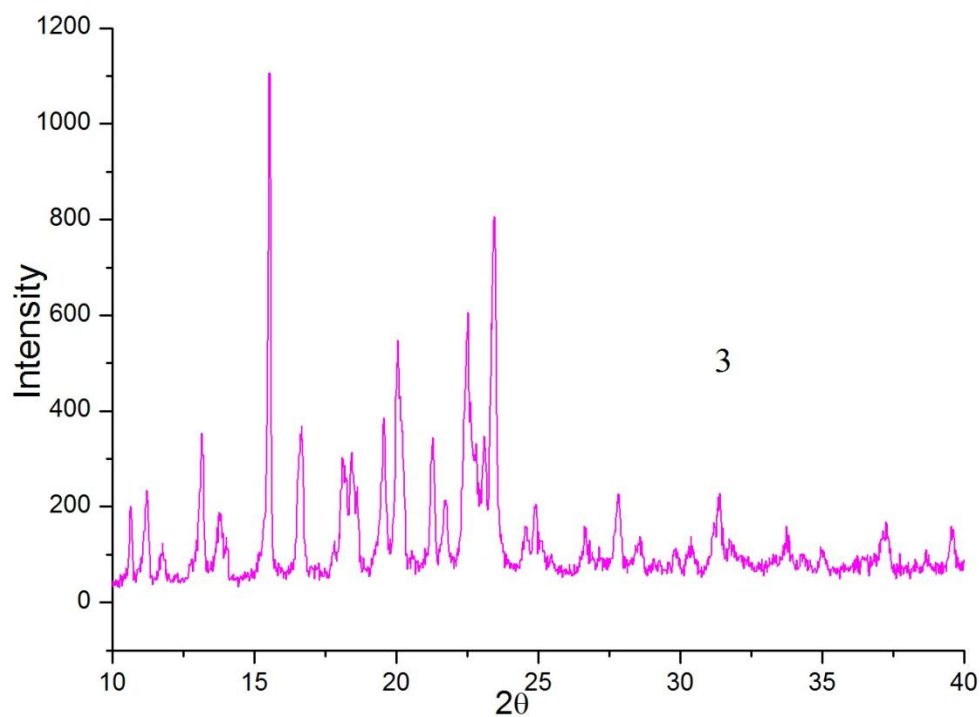


Figure S 8. Powder XRD of 3 (Calculated):

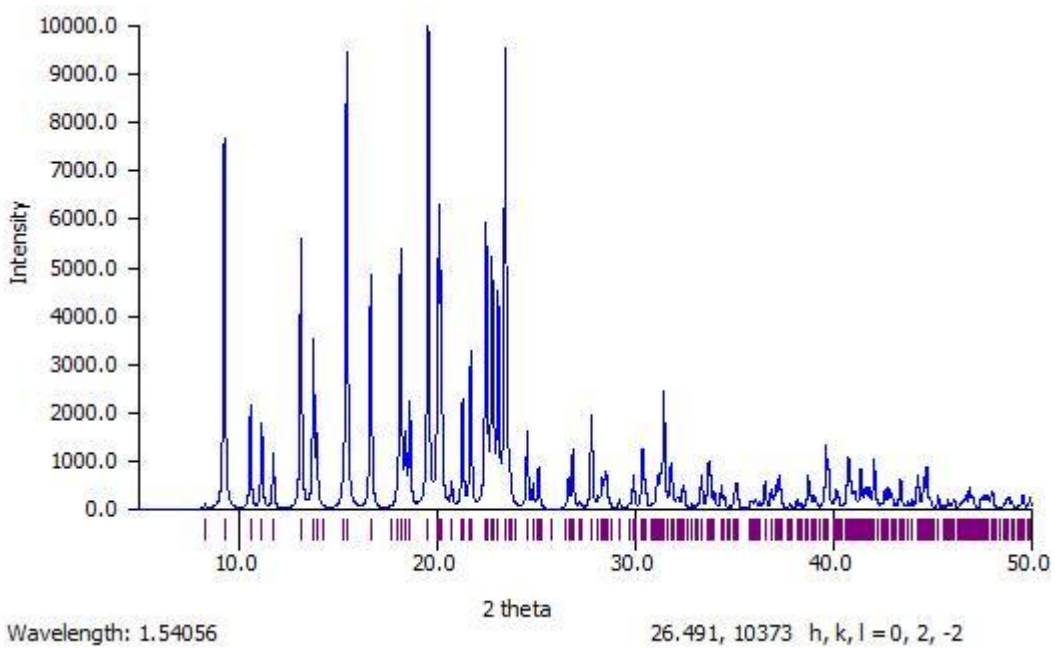


Figure S 9. Powder XRD of 4a:

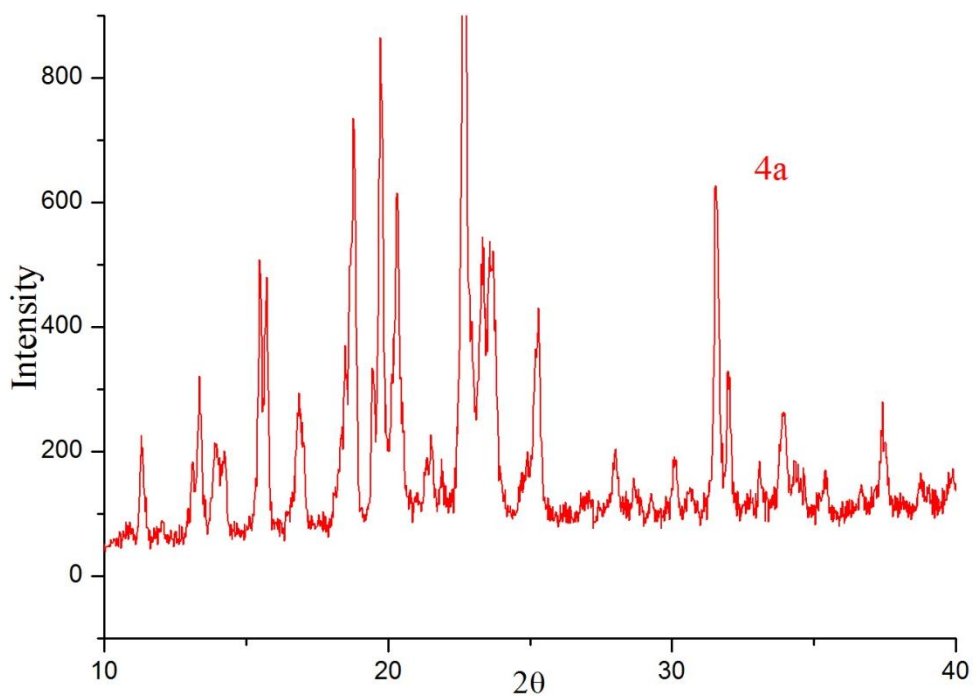


Figure S 10. Powder XRD of 4b:

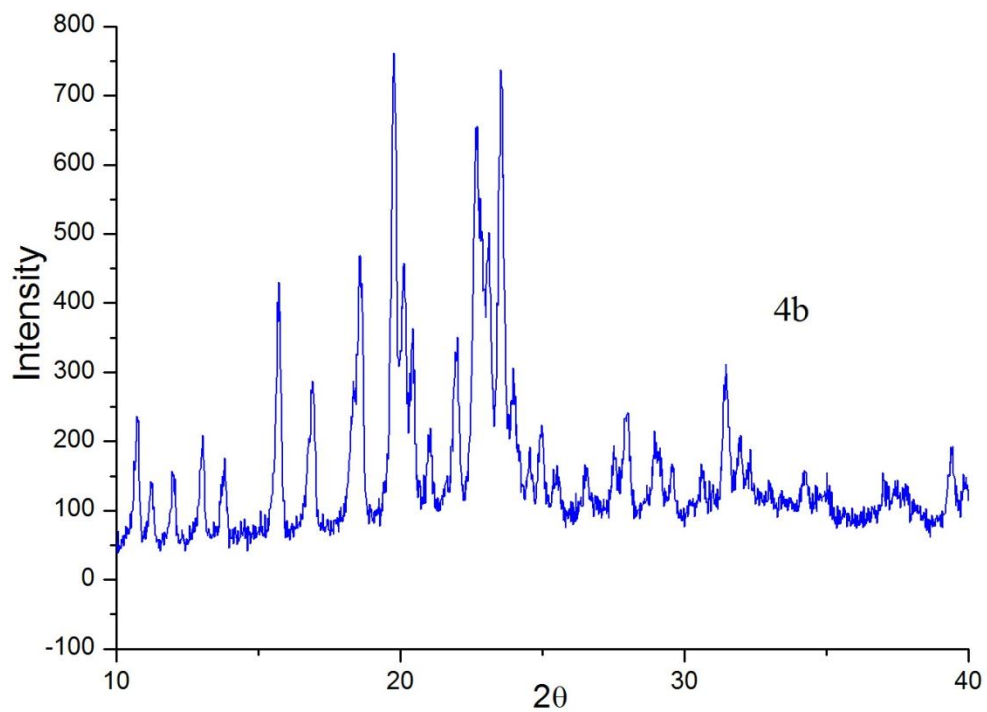


Figure S 11. Powder XRD of 4c:

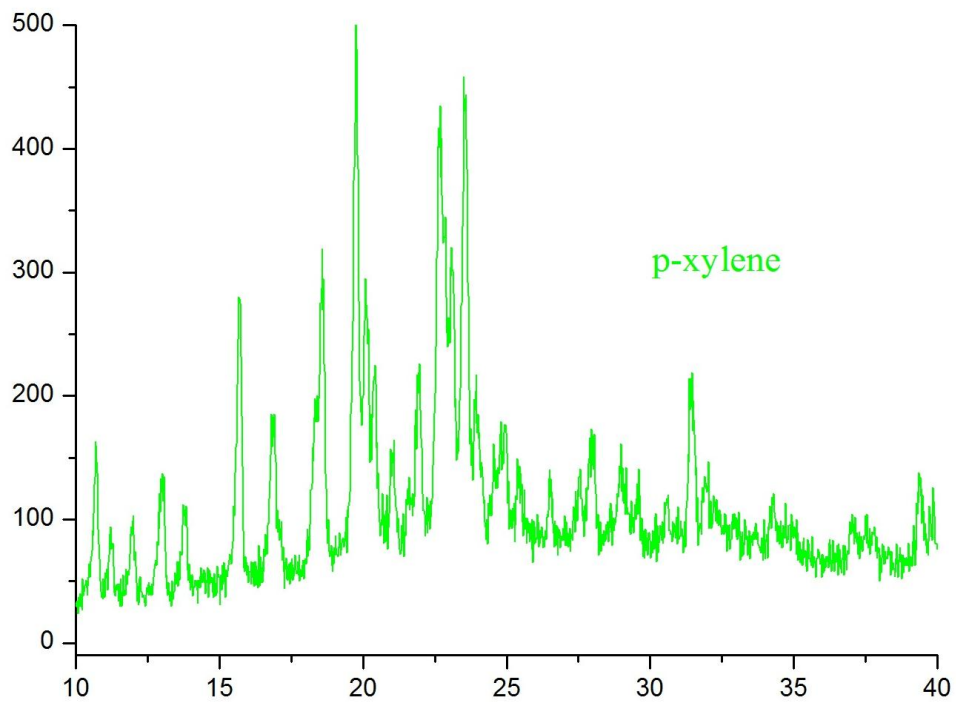


Figure S 12. Powder XRD of Apohost 4:

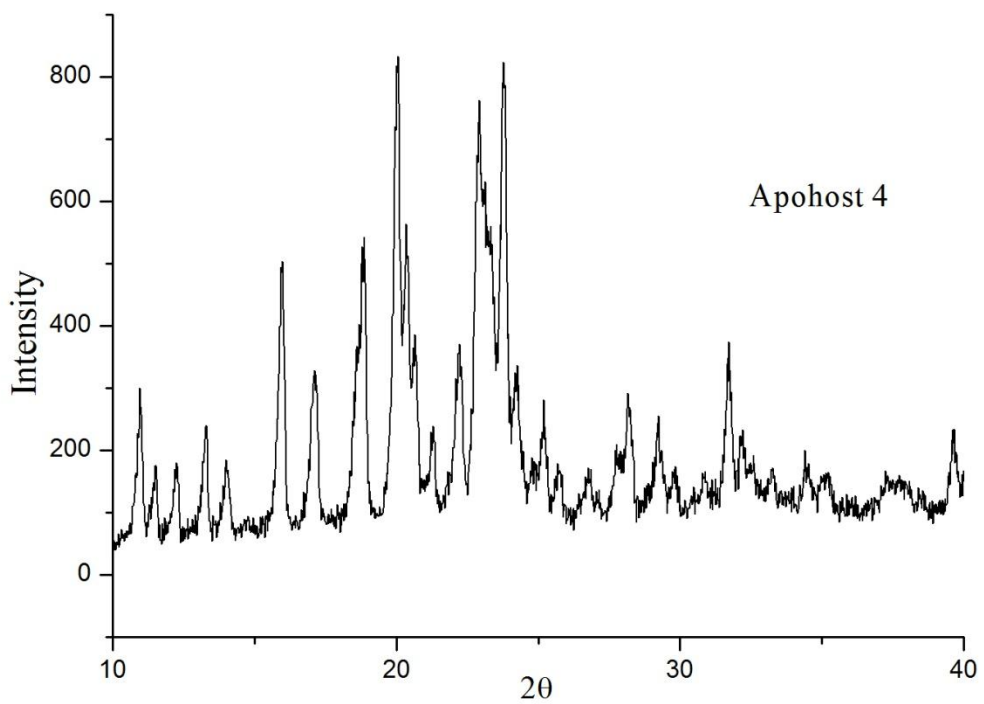


Figure S 13. Solid State UV-Vis Spectra of Ligand 1a

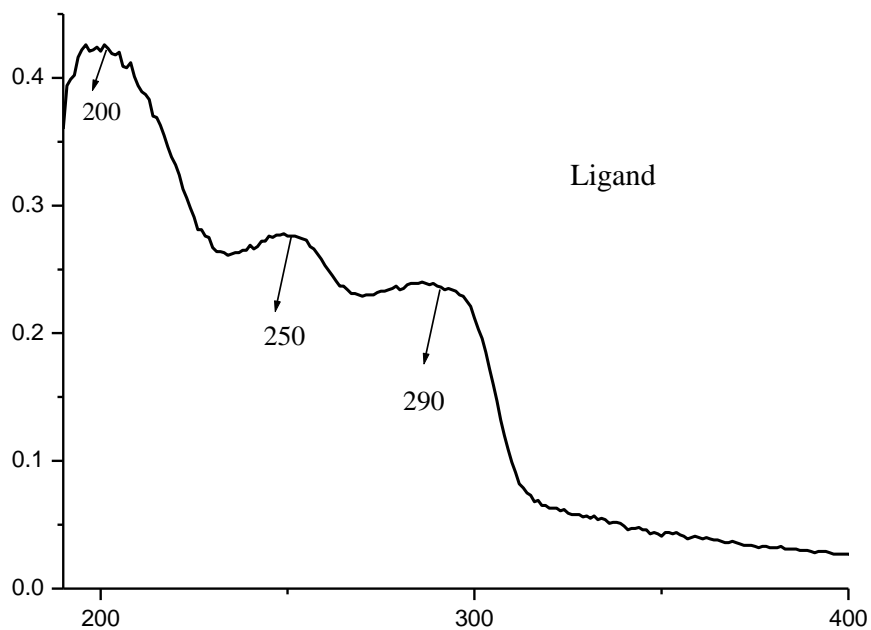


Figure S 14. Solid State UV-Vis Spectra of 3

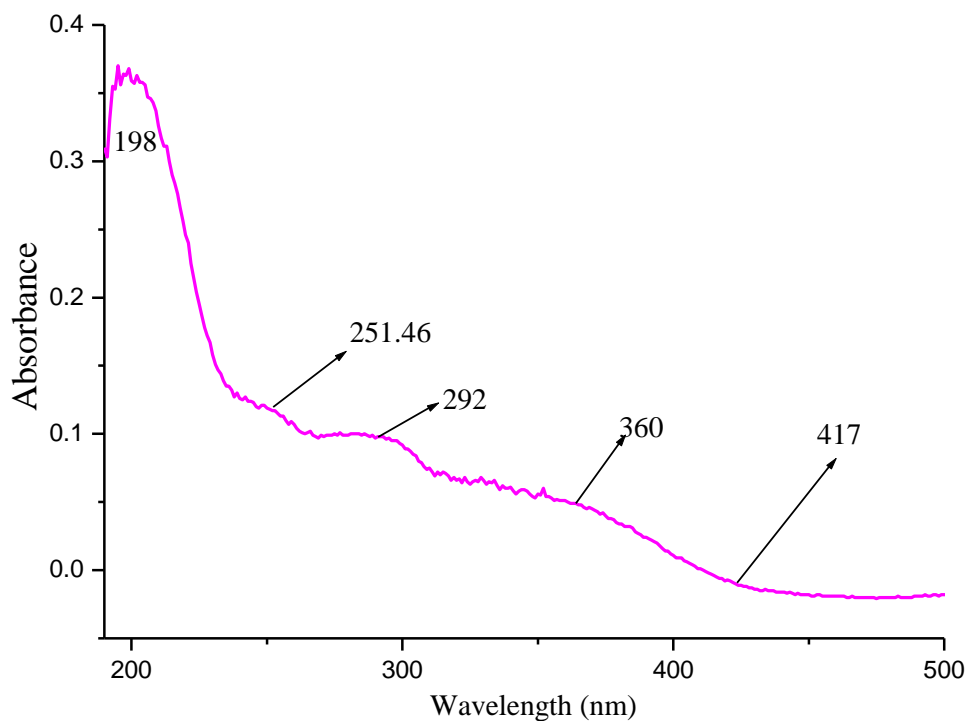


Figure S 15. Solid State UV-Vis Spectra of Apohost 4:

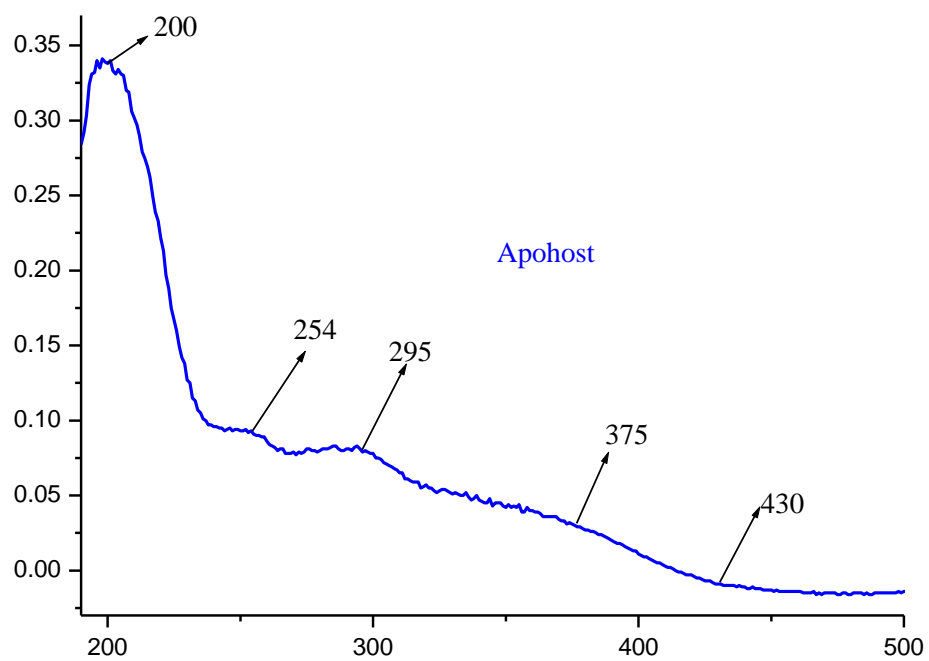


Figure S 16. Solid State UV-Vis Spectra of 4a:

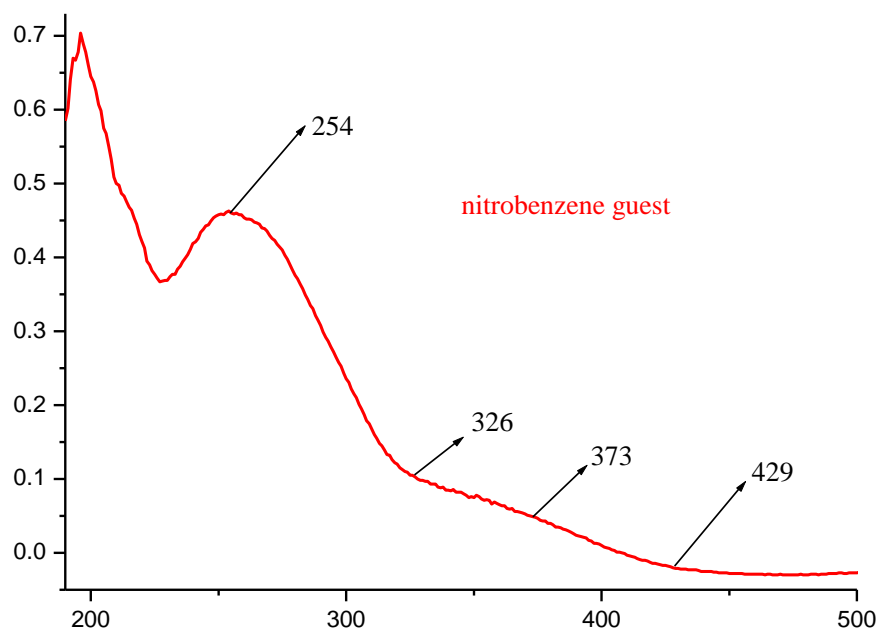


Figure S 17. Solid State UV-Vis Spectra of 4b:

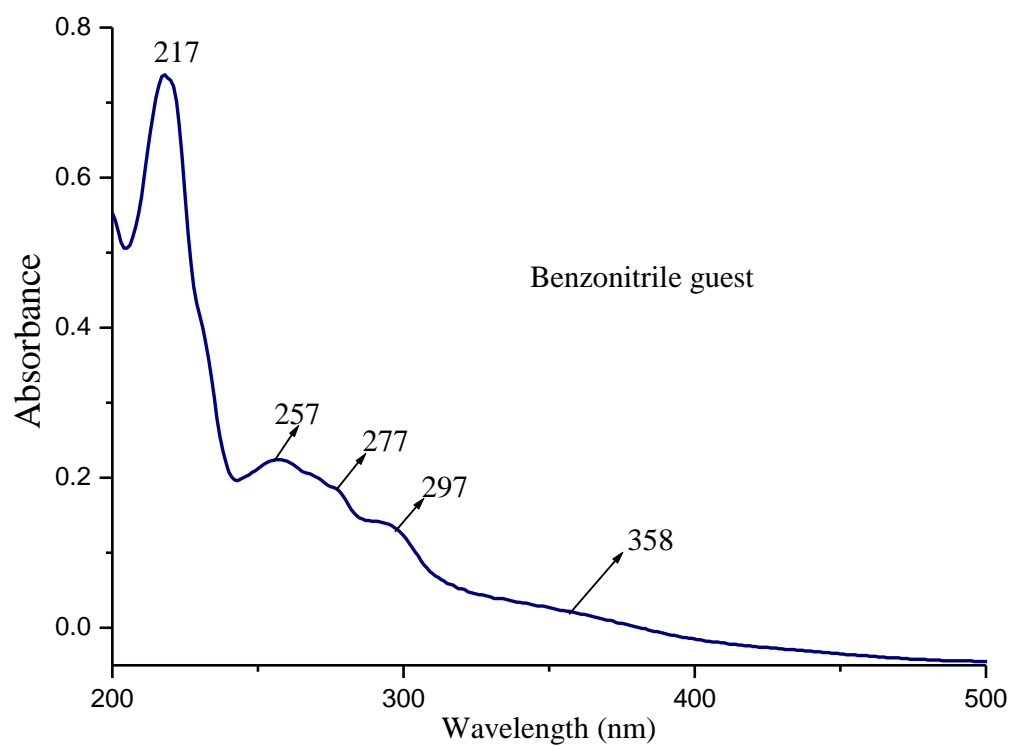


Figure S 18. UV-Vis Spectra of known concentrations of nitrobenzene (λ_{max} at 262 nm):

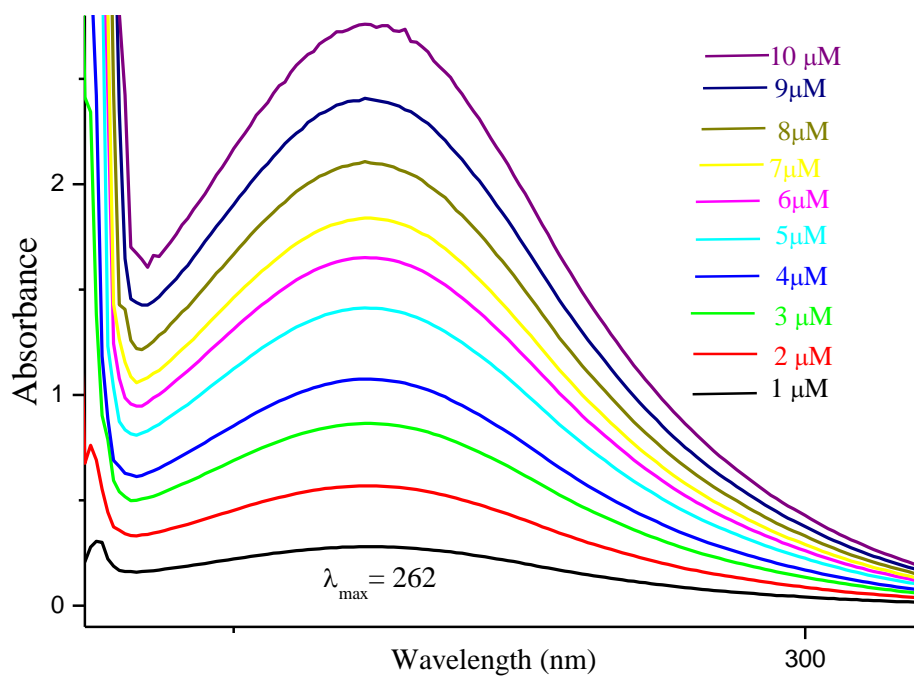


Figure S 19. Calibration plot of nitrobenzene (Absorbance vs. Conc)

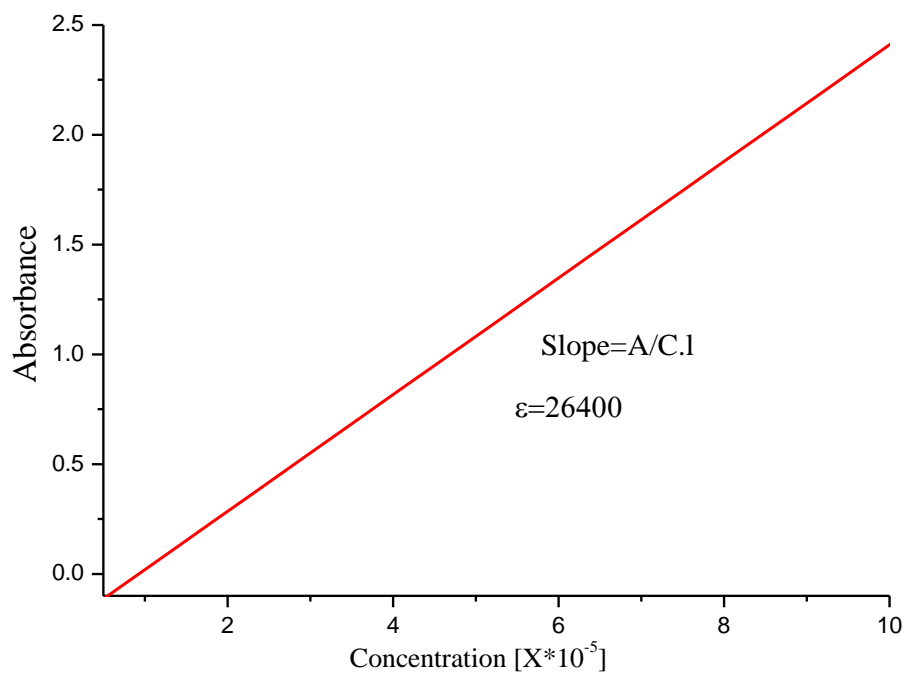


Figure S 20. Extracting nitrobenzene in chloroform from known amount of **4a**

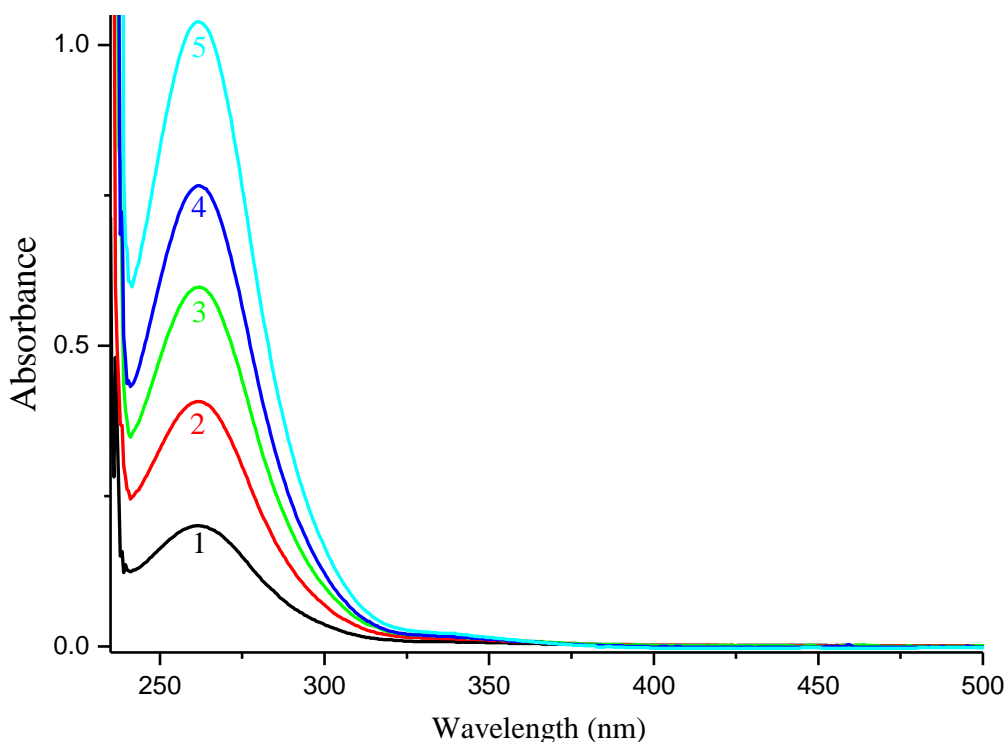


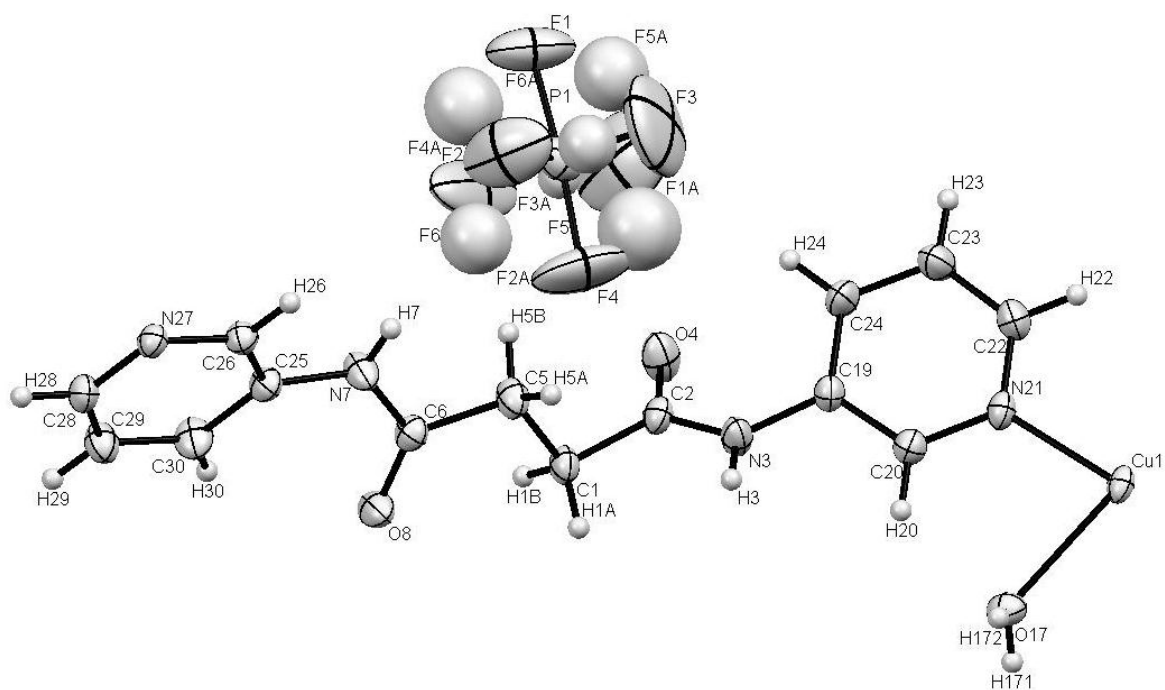
Table S 1.

Plot no.	Wt. of MOF	Nitrobenzene conc. (molar) $C=A/\epsilon.l$	No. of Molecules of Nitrobenzene**
1	0.00237 gm	$0.761 \times 10^{-5} M$	2.694004
2	0.00475 gm	$0.154 \times 10^{-4} M$	2.720126
3	0.00712 gm	$0.207 \times 10^{-4} M$	2.439228
4	0.00952 gm	$0.290 \times 10^{-4} M$	2.555777
5	0.01190 gm	$0.393 \times 10^{-4} M$	2.770815

** Assuming the molecular weight of Apohost **4** = Cu +2 Ligand + 2 Coordinated H₂O + 2ClO₄⁻ = 63.5 + (2 × 270) + (2 × 18) + (2 × 99.5)=838.5 gm

Five sets of above given weight **4a** was taken in 10ml of chloroform and stirred overnight at RT. Then UV-Vis spectra were recorded for these five sets of extracted nitrobenzene in Chloroform. Using Lambert-Beer's Law, concentration of nitrobenzene was calculated.

Figure S 21. ORTEP of 3:



References:

1. *CrysAlis PRO* (Oxford Diffraction, 2010, Oxford Diffraction Ltd., Yarnton, Oxfordshire, England)
2. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.
3. (a) M. Sarkar and K. Biradha, *Cryst. Growth Des.*, 2006, **6**, 202; (b) L. Rajput, S. Singha and K. Biradha, *Cryst. Growth Des.*, 2007, **7**, 2788.