Supporting Information

Coordination-Driven Self-Assembly of Cyclopentadienyl Capped Heterometallic Zr−Pd Cages

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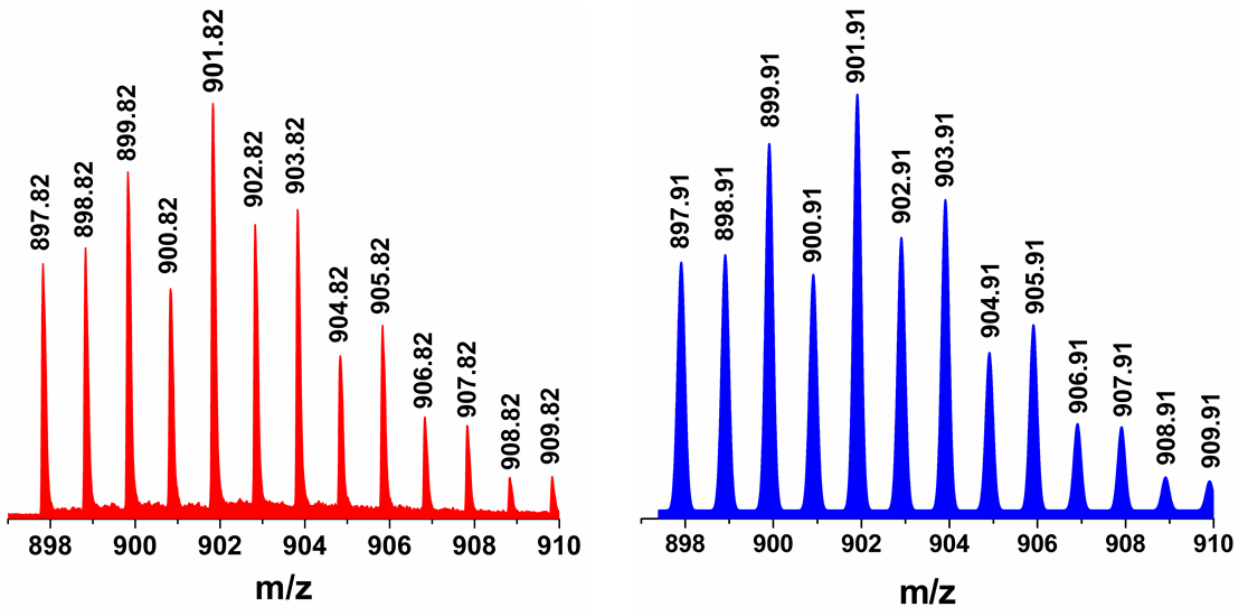

Figure. S1: Experimental (red) and calculated (blue) HRMS-ESI spectra of **L^1.**

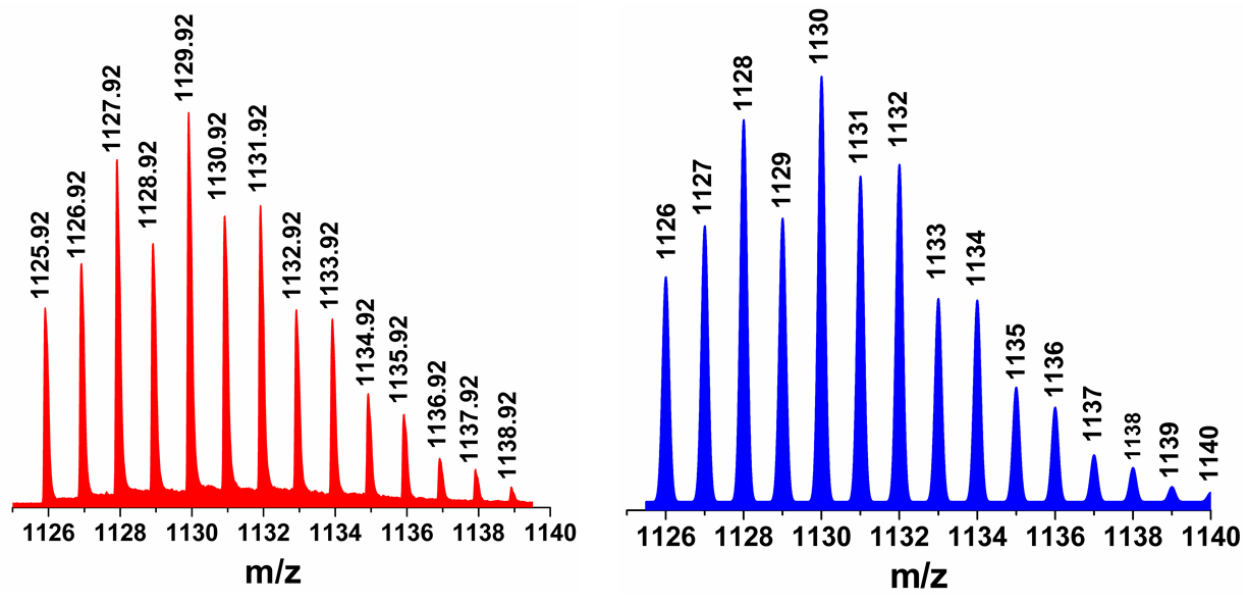

Figure. S2: Experimental (red) and calculated (blue) HRMS-ESI spectra of **L^2.**

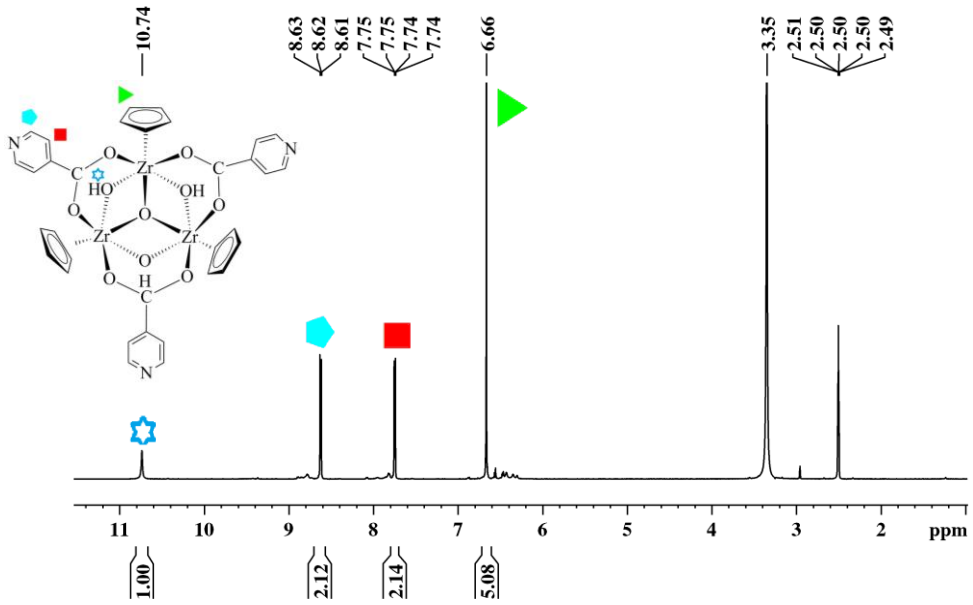

Figure S3: The ^{1}H-NMR spectrum of ligand **L^{1}** at DMSO-d$_6$ solvent.

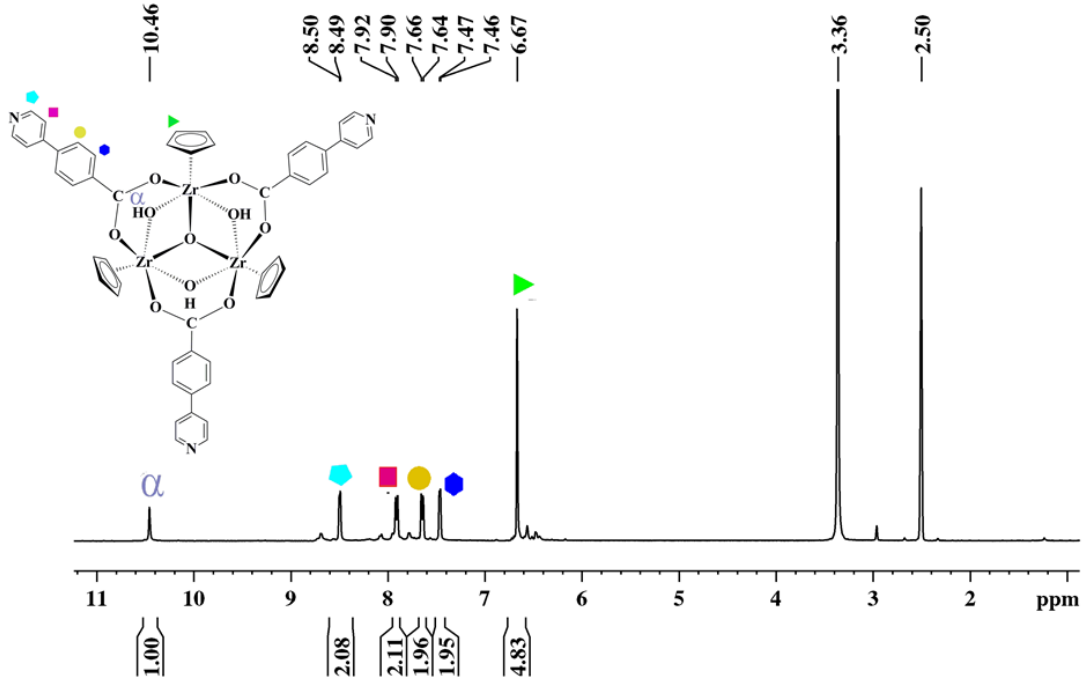

Figure S4: The ^{1}H-NMR spectrum of ligand **L^{2}** at DMSO-d$_6$ solvent.

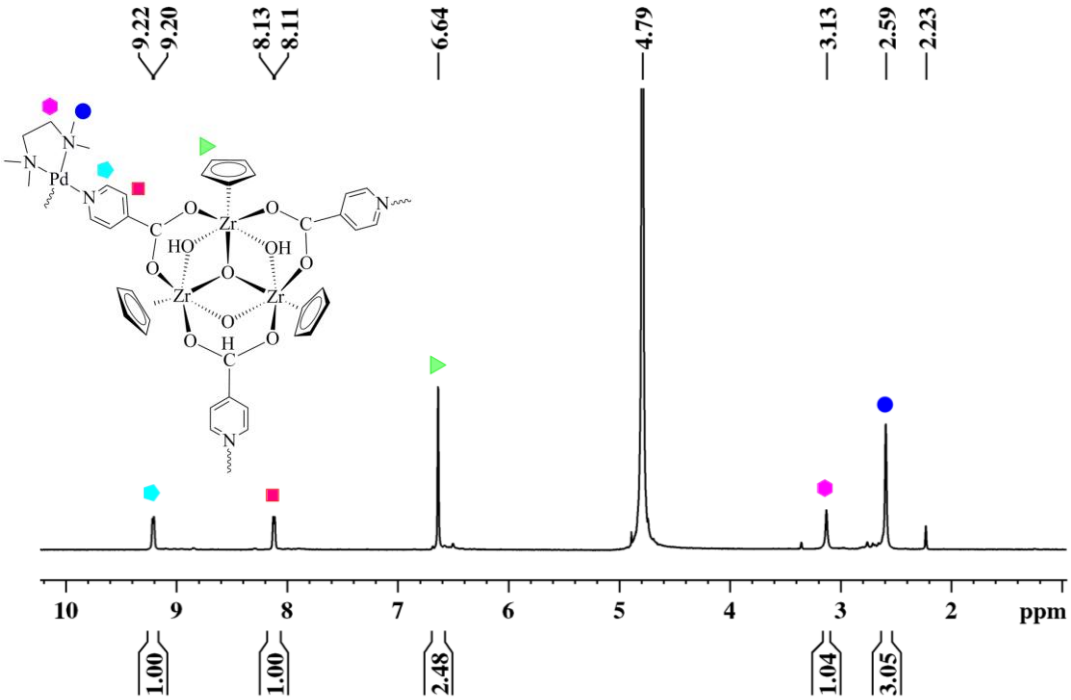

Figure S5: The ^{1}H-NMR spectrum of compound **1** at D_2O solvent.

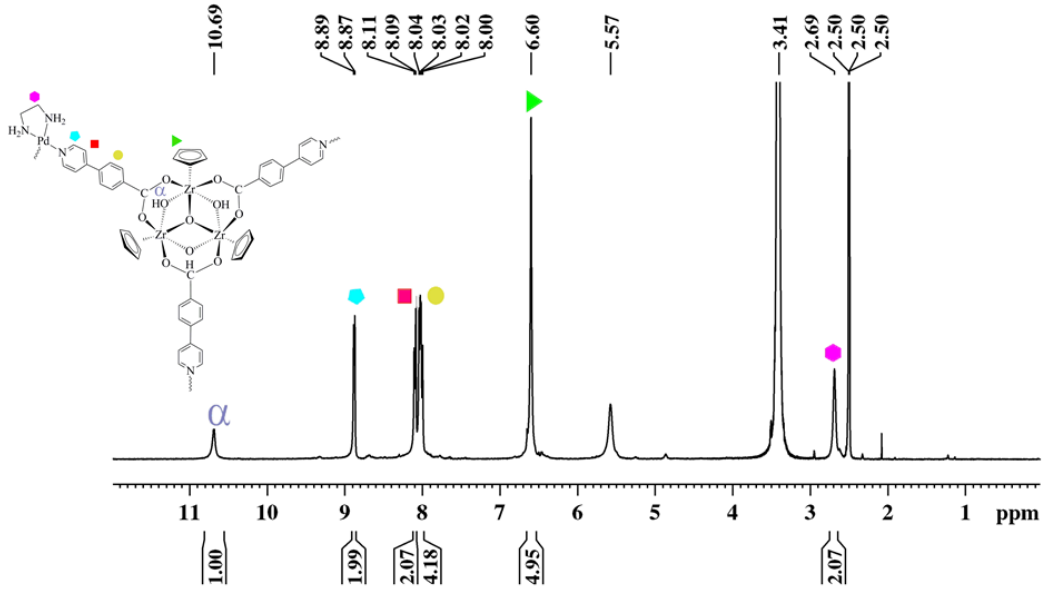

Figure S6: The ^{1}H-NMR spectrum of compound **4** at DMSO-d_6 solvent.

Host-guest interaction of compound 2 with naphthalene. A series of 5 mM solutions of compound 2 in the mixture of solvents D_2O and CD_3OD (1:1) containing varying amounts of naphthalene, ranging from 1 mM to 20 mM, were prepared and were examined by ^1H NMR spectroscopy (27 °C). The mole ratio method[1] was applied, and the stoichiometry of the association was found to be two guest molecules per one molecule of host (Figure S8). Equilibrium constants were determined using a previously described algorithm.[2] This procedure yielded values of K_1(Compound 2: Naphthalene) = 1120 ± 27 M^{-1} and K_2 (Compound 2: Naphthalene) = 96 ± 12 M^{-1}.

Host-guest interaction of compound 2 with 2-naphthaldehyde. The host-guest association constants for cage 2 and 2-naphthaldehyde in mixture of solvents D_2O and CD_3OD (1:1) solution at 27 °C was determined by the ^1H NMR titration method. A series of 5 mM solutions of compound 2 in mixture of solvents D_2O and CD_3OD (1:1) containing varying amounts of 2-naphthaldehyde, ranging from 1 mM to 20 mM, were used. The stoichiometry of the association was found to be two guest molecules per one host molecule (Figure S13). The maximum chemical shift change for any of the protons of the host was 0.11 ppm (pyridyl α-H). The maximum chemical shift change observed for the guest was 0.2 ppm, with others chemical shift changing by about 0.2 ppm. The data were analyzed using a curve fitting procedure and yielded values of K_1 (Compound 2: 2-Naphthaldehyde) = 2488 ± 41 M^{-1} and K_2 (Compound 2: 2-Naphthaldehyde) = 310 ± 32 M^{-1}).

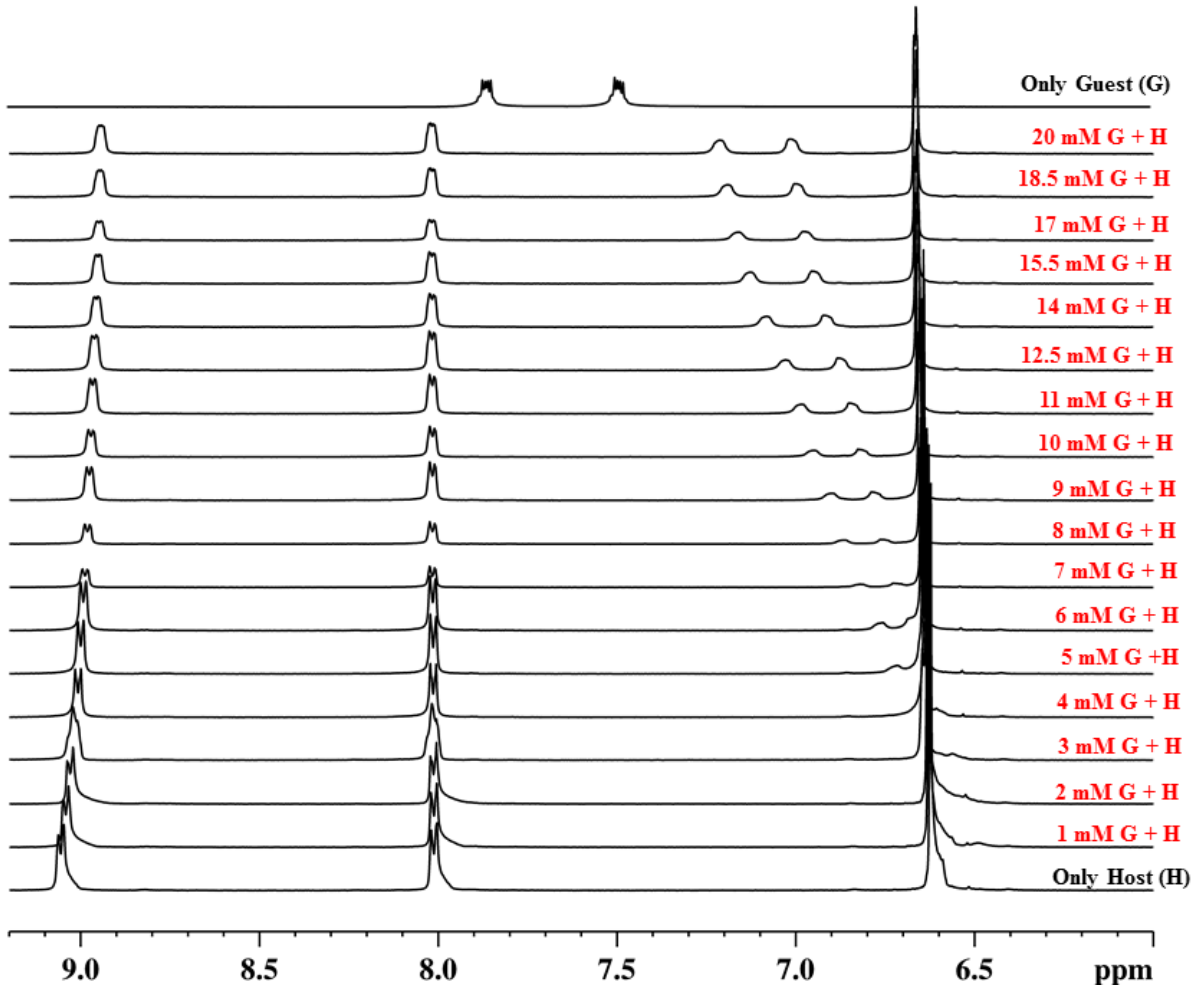

Figure S7: ^{1}H NMR titration for the host-guest complex formed between compound **2** and naphthalene. The experiments were performed at 27°C in D_2O + CD_3OD (1:1) with the concentration of compound **2** held constant at 5 mM and the concentration of naphthalene varied between 1 mM to 20 mM. The plot refers to the pyridyl α-proton of host. The bottom and top ^{1}H NMR are for only host and only guest respectively.

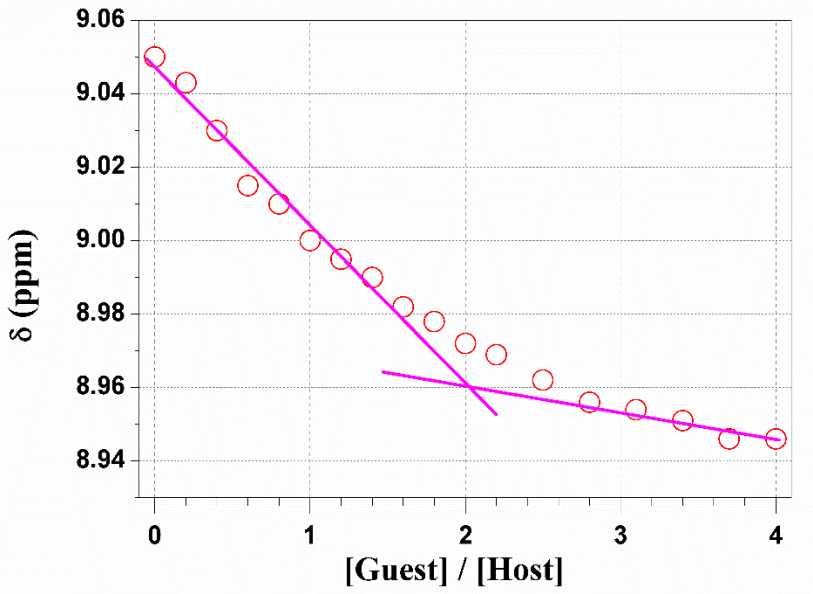

Figure S8: ^{1}H NMR stoichiometry titration for the host-guest complex formed between compound **2** and naphthalene. The experiments were performed at 27°C in D_2O + CD_3OD (1:1) with the concentration of compound **2** held constant at 5 mM and the concentration of naphthalene varied between 1 mM to 20 mM.

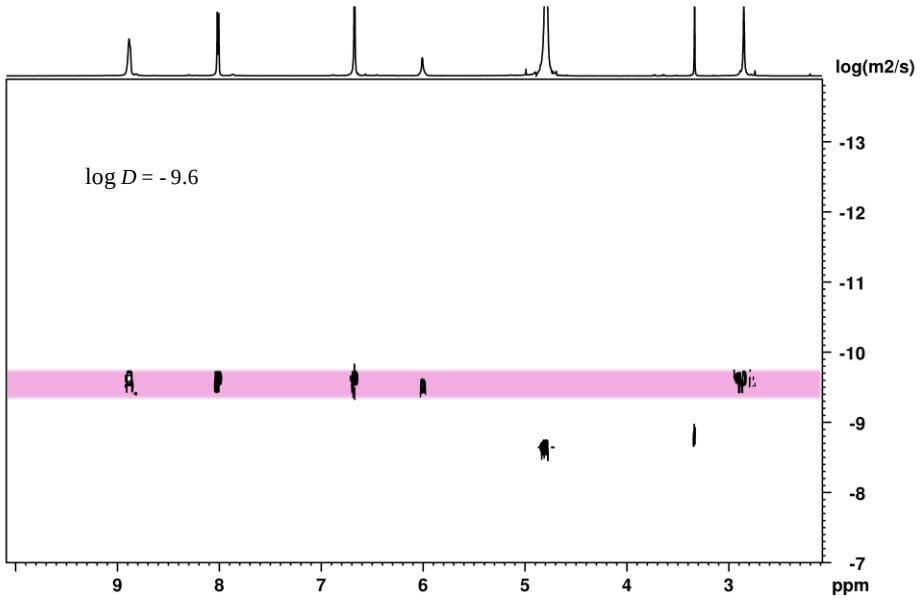

Figure S9: ^{1}H – ^{1}H DOSY spectrum of naphthalene encapsulated compound **2** (300 K, D_2O).

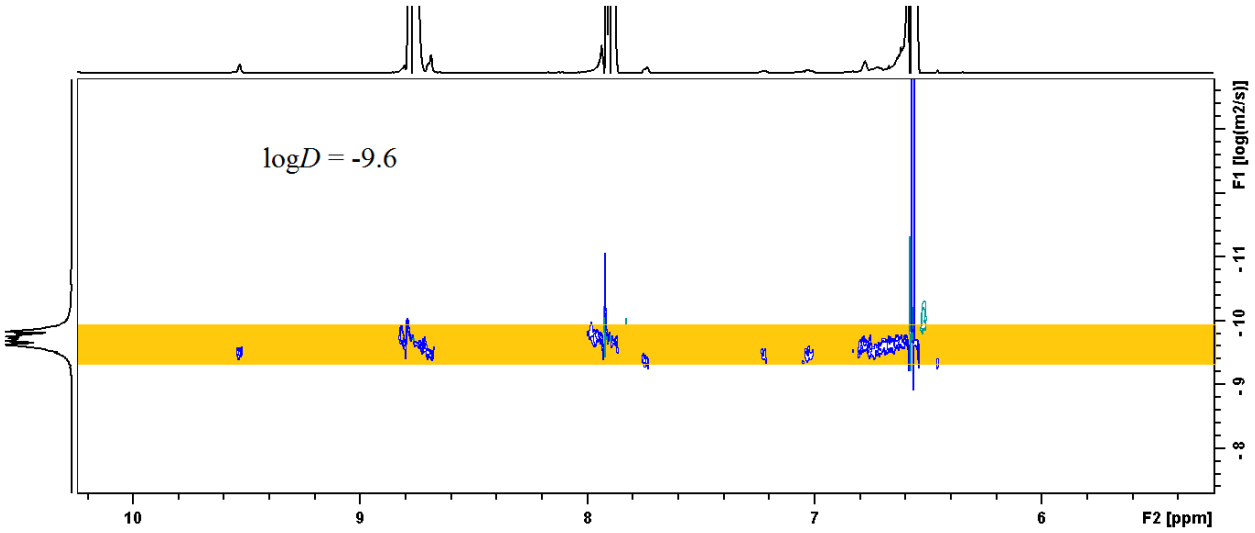

Figure S10: $^{1}H - {}^{1}H$ DOSY spectrum of 2-naphthaldehyde encapsulated compound **2** (300 K, D_2O).

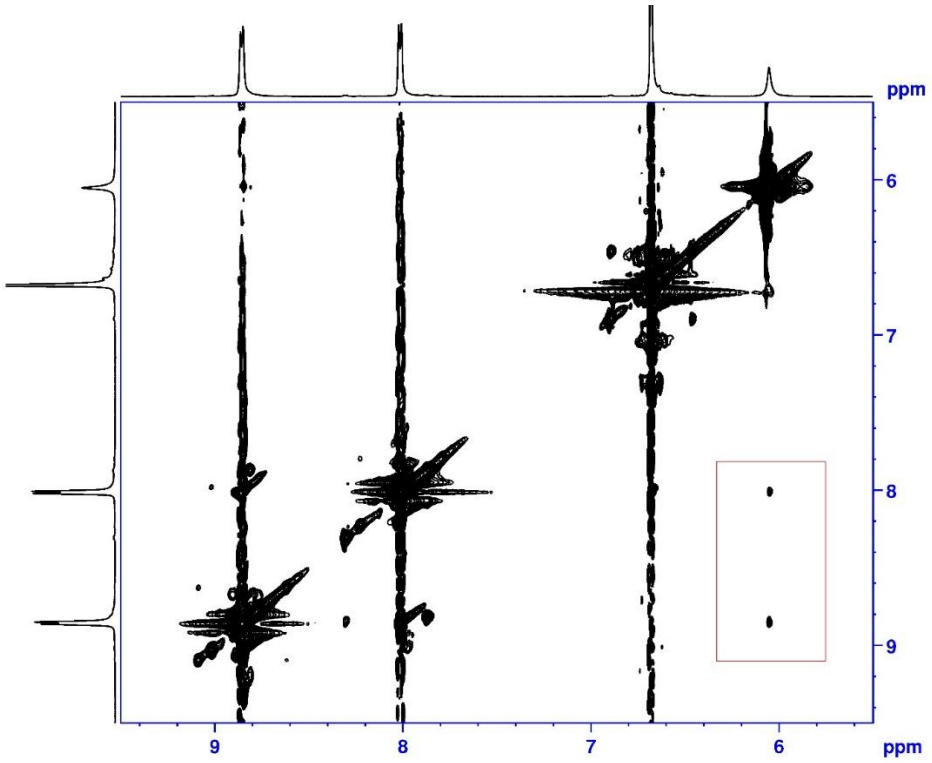

Figure S11. NOESY (400 MHz, D_2O, 300 K) spectrum of compound **2** encapsulated naphthalene guests. The magenta color box highlights NOE interactions between encapsulated naphthalene with the compound **2** host pyridyl α and β protons.

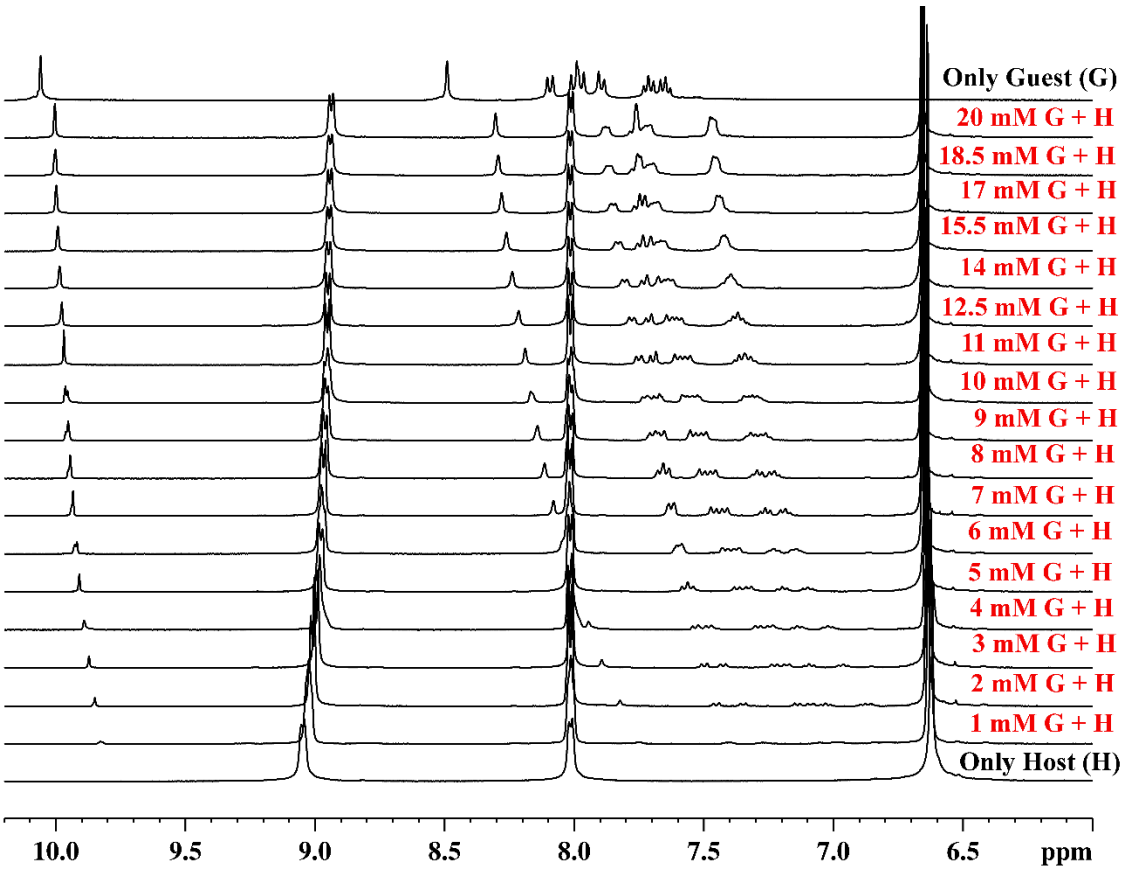

Figure S12: ^{1}H NMR titration for the host-guest complex formed between compound **2** and 2-naphthaldehyde. The experiments were performed at 27°C in D_2O + CD_3OD (1:1) with the concentration of compound **2** held constant at 5 mM and the concentration of 2-naphthaldehyde varied between 1 mM to 20 mM. The plot refers to the pyridyl α-proton of host. The bottom and top ^{1}H NMR are for only host and only guest respectively.

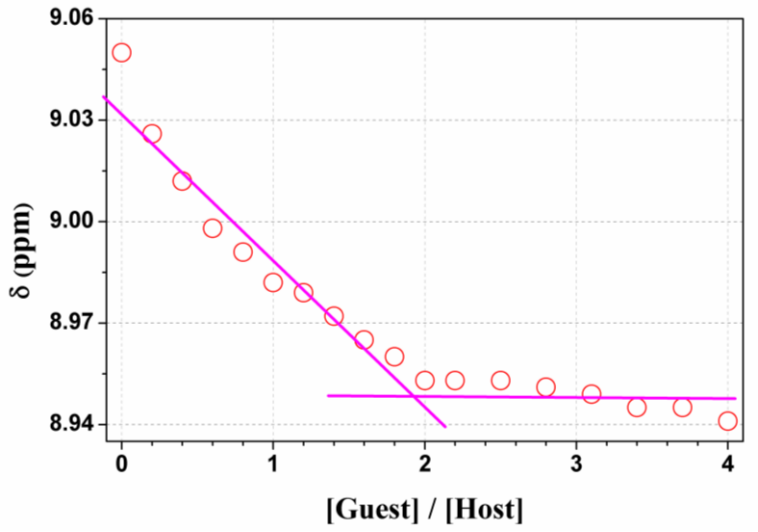

Figure S13: ^{1}H NMR stoichiometry titration for the host-guest complex formed between compound **2** and 2-naphthaldehyde. The experiments were performed at 27°C in D_2O + CD_3OD (1:1) with the concentration of compound **2** held constant at 5 mM and the concentration of 2-naphthaldehyde varied between 1 mM to 20 mM.

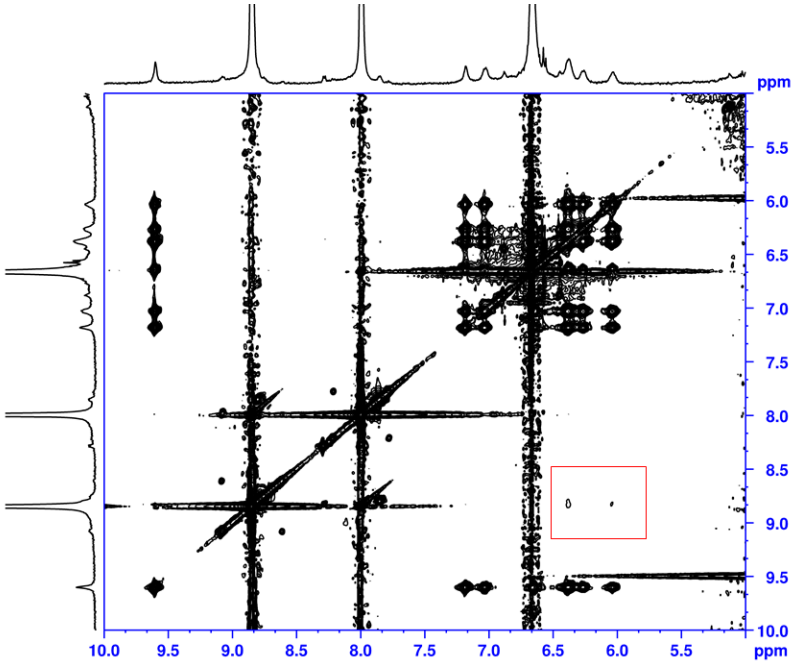

Figure 14. NOESY (400 MHz, D_2O, 300 K) spectrum of compound **2** encapsulated 2-naphthaldehyde guest. The red box highlights NOE interactions between encapsulated 2-naphthaldehyde with the cage 2 host pyridyl α protons.

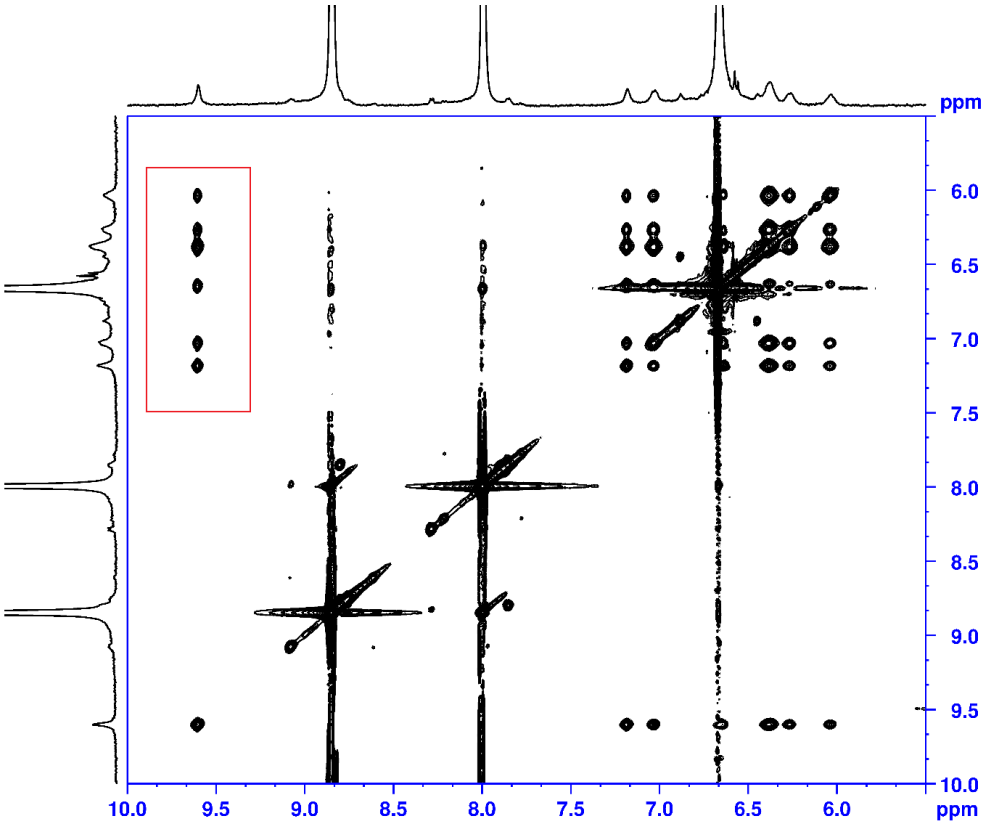

Figure 15. Enlarged NOESY spectrum (500 MHz, D_2O, 300 K) of the encapsulated 2-naphthaldehyde in the compound **2**. The red box highlights intermolecular NOE interactions of the host and guest.

Table S1: Thermodynamic data for host-guest adducts.

Host	**Guest**	**Host-Guest Ratio**	**Solvent**	**T(K)**	**Binding Constants (M^{-1})**	**ΔG (kcal/mole)**
Compound 2	Naphthalene	1:2	1:1(D_2O:CD_3OD)	300	K_1 = 1120 ± 27 K_2= 96 ± 12	-4.185 -2.72
Compound 2	2-Naphthaldehyde	1:2	1:1(D_2O:CD_3OD)	300	K_1 = 2488 ± 41 K_2= 310 ± 32	-4.661 -3.42

Table S2: The crystal data and structure solution parameters of compound **4** .

Crystal System	hexagonal
Space group	P 63/m
a, Å	19.655(7)
b, Å	19.655(7)
c, Å	30.201(10)
α, deg	90
β, deg	90
γ, deg	120
V, $Å^3$	10104(8)
δ(g/cm−3)	0.901
Temp, K	110
λ (Mo $K_α$), Å	0.71073
Z	2
Mu(mm^{-1})	0.595
F(000)	2720
Reflections Collected/Unique	242490/4901
R	0.2145
GOF	1.975
wR2	0.4886
Δ ρ max/min/e $Å^3$	4.08, -416

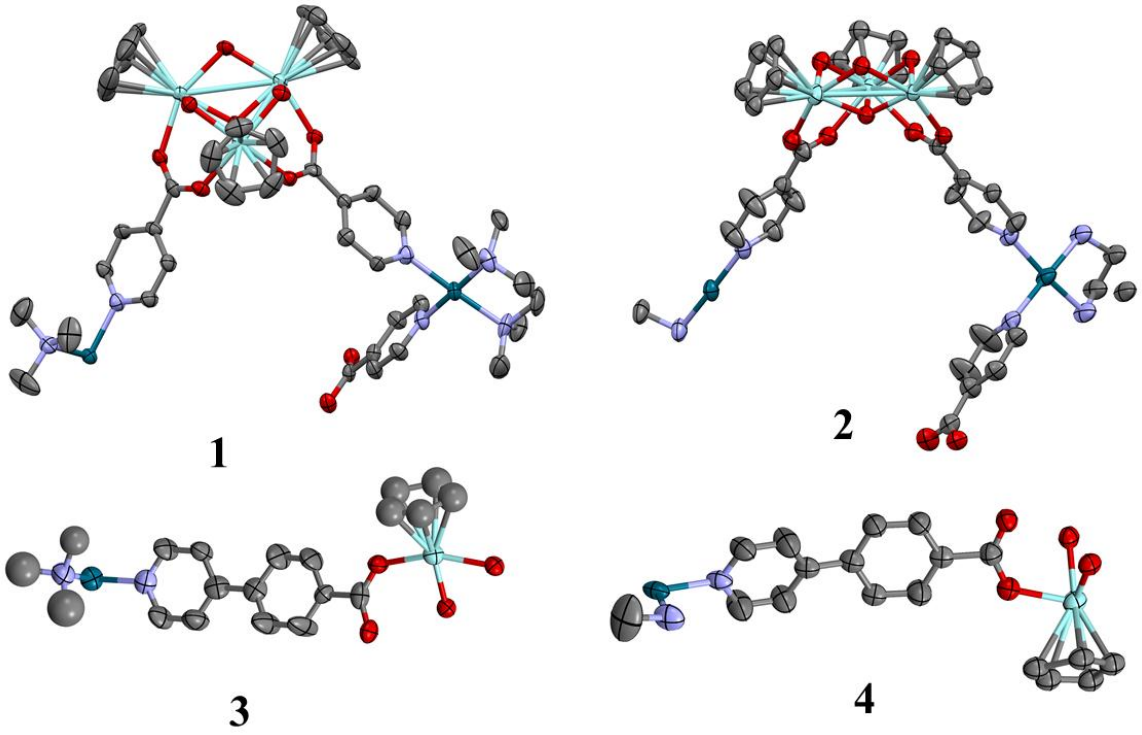

Fig.S16. Thermal ellipsoid drawing at 50% probability of the asymmetric unit of the compounds **1 – 4**. Hydrogen atoms, solvent molecules and anions have been omitted for clarity. Color codes: Pd = green, Zr = sky blue, N = blue, C = gray, and O = red.

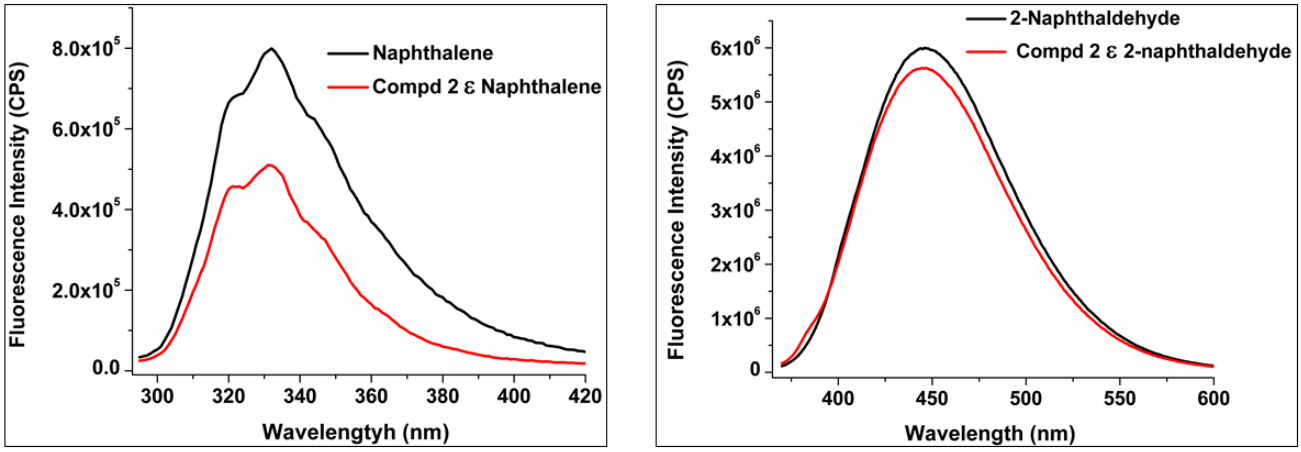

Fig.S17. Luminescence spectra of guests (naphthalene & 2-naphthaldehyde) before encapsulation (black line) and after encapsulation (red line) into the compound **2** in purely aqueous medium.

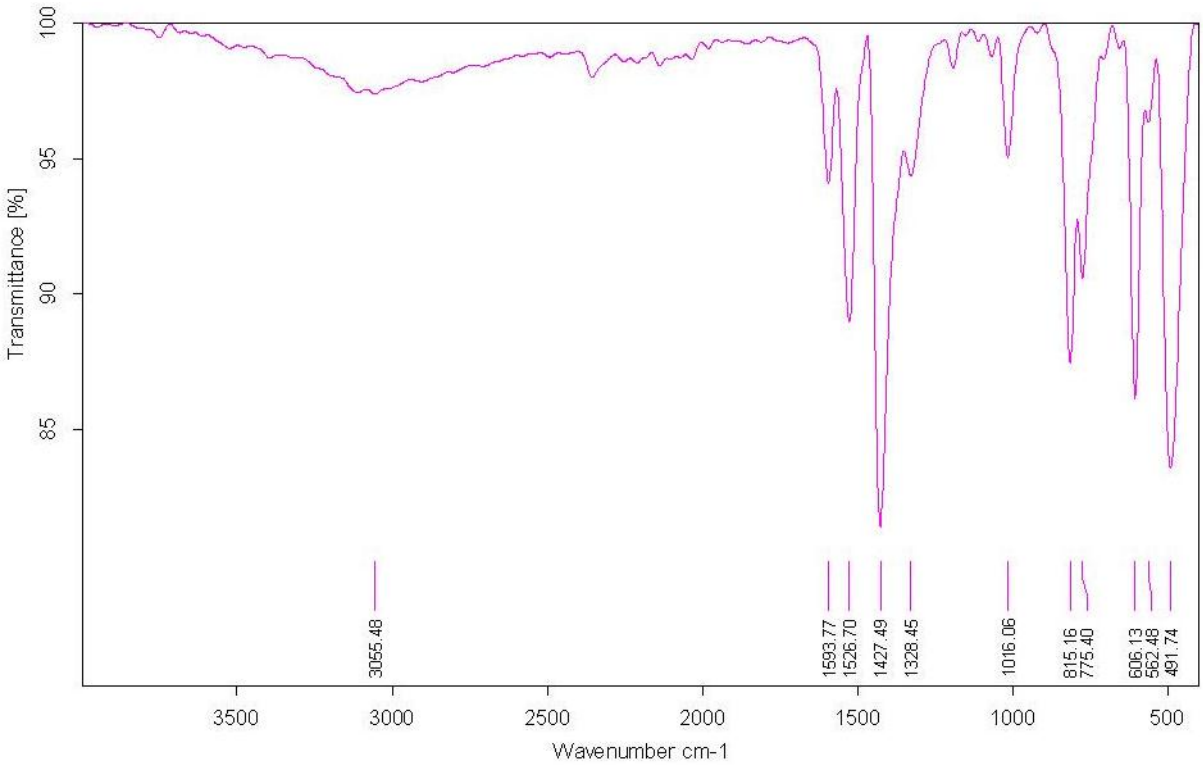

Figure S18: The FT-IR spectrum of ligand $\mathbf{L^1}$.

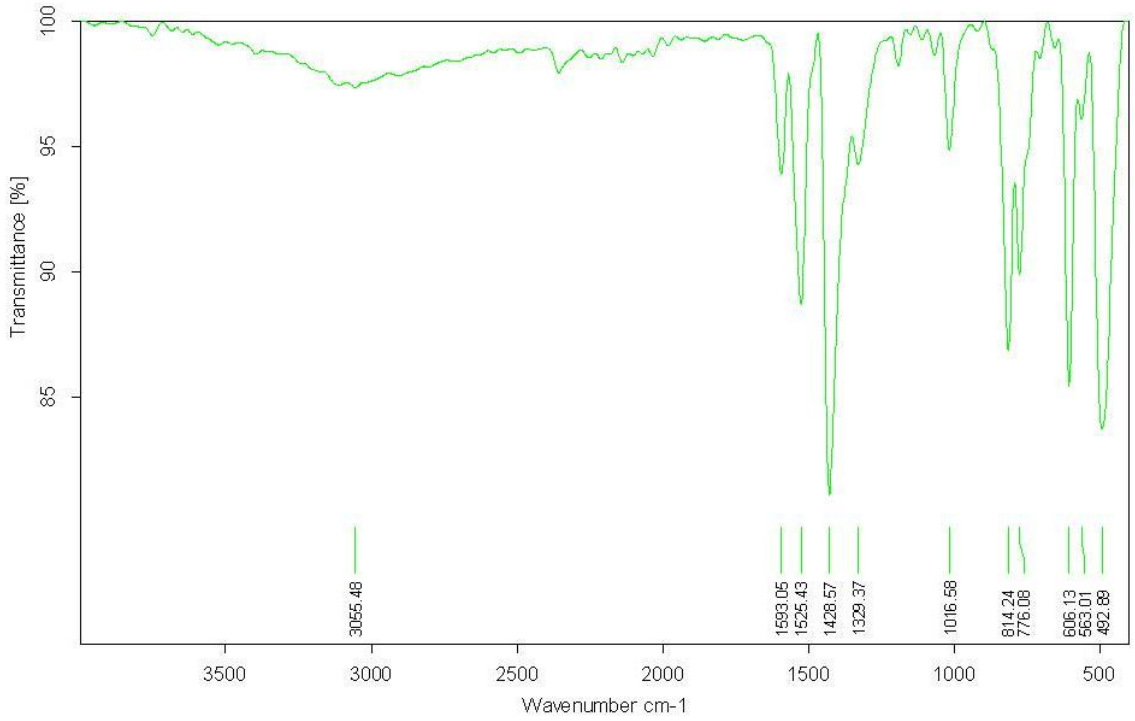

Figure S19: The FT-IR spectrum of ligand **L^2.**

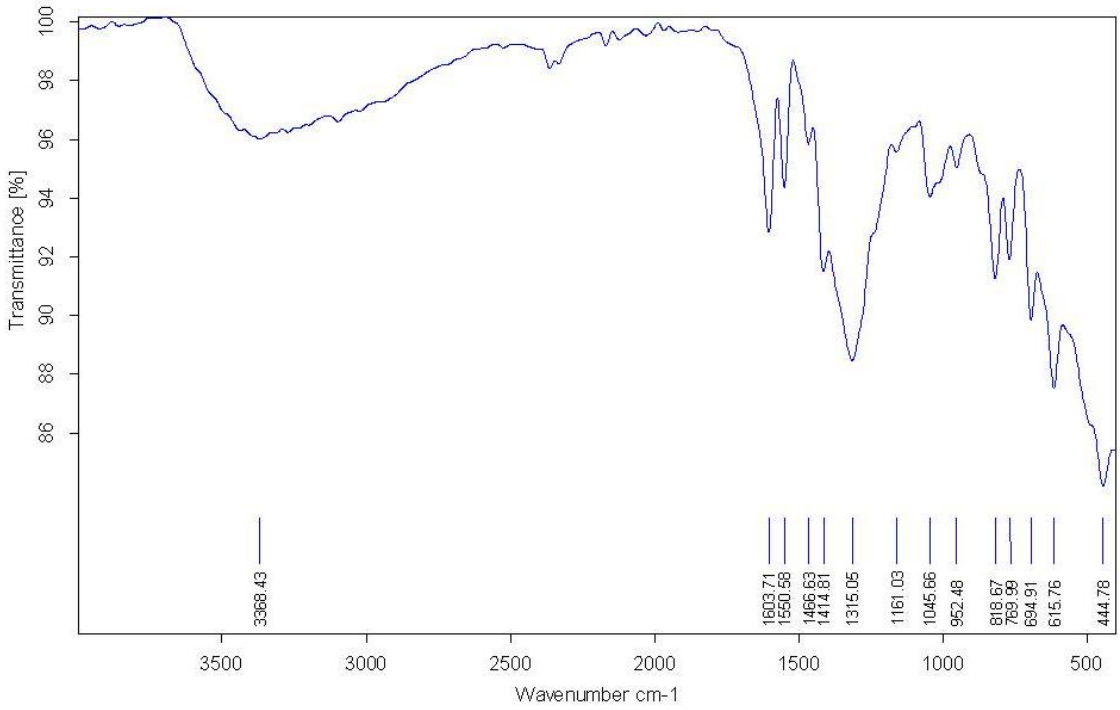

Figure S20: The FT-IR spectrum of compound **1**.

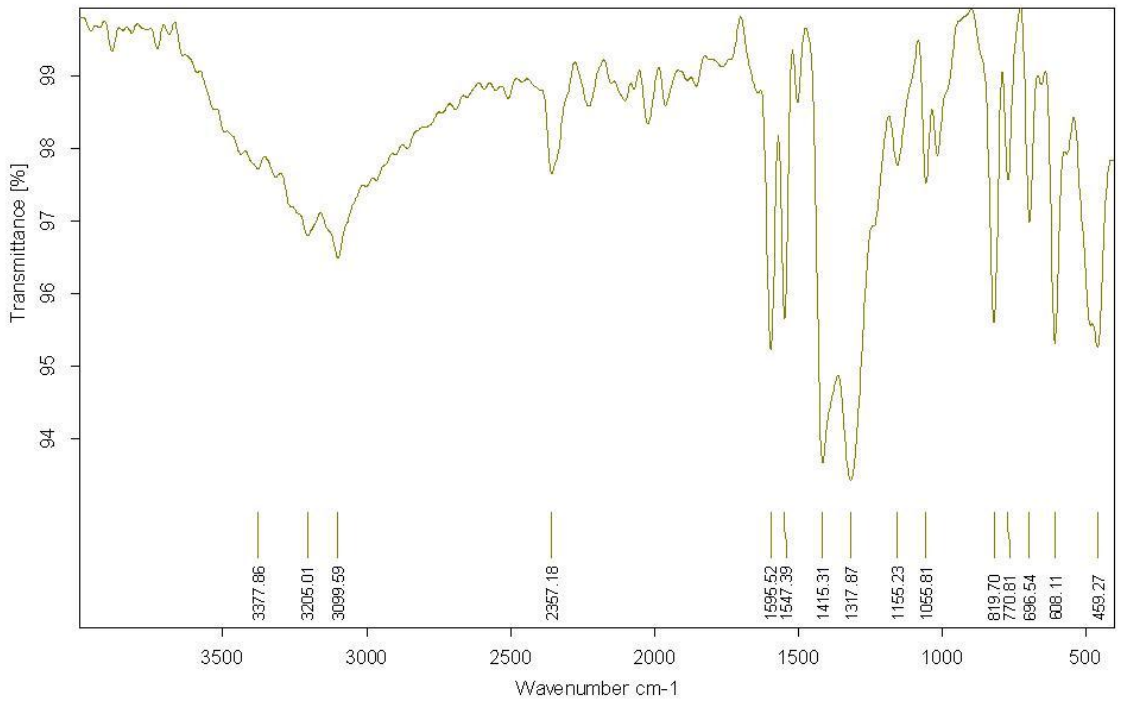

Figure S21: The FT-IR spectrum of compound **2**.

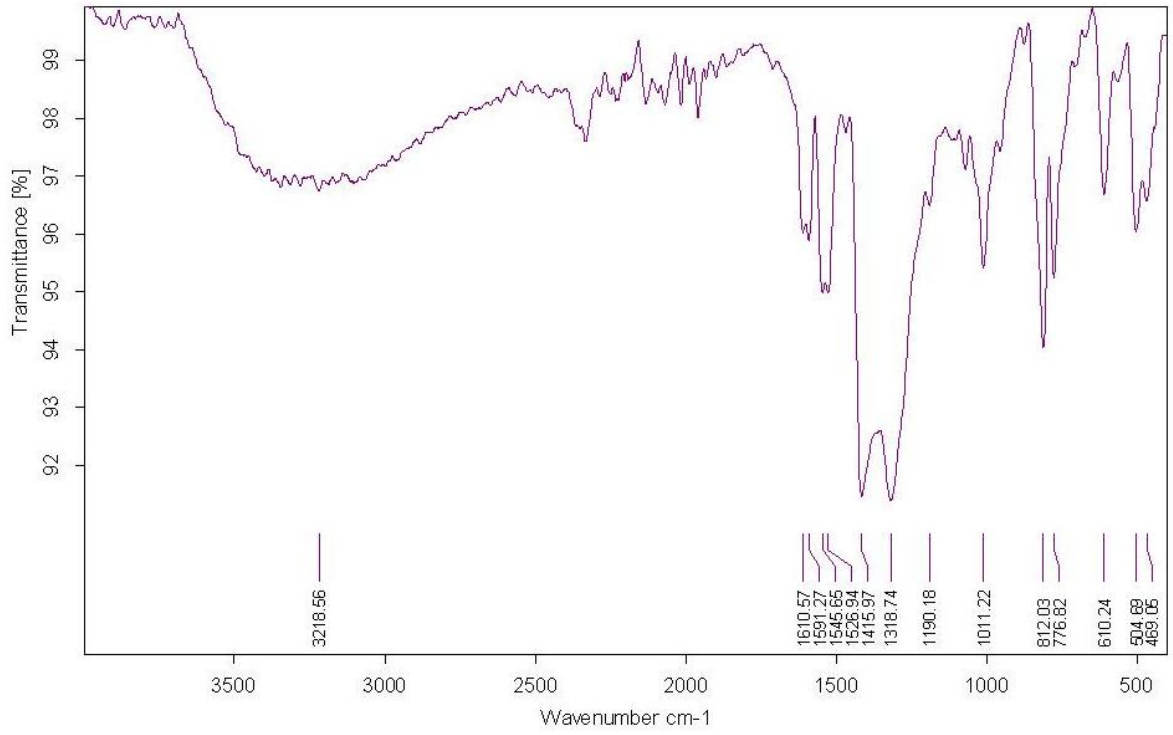

Figure S22: The FT-IR spectrum of compound **3**.

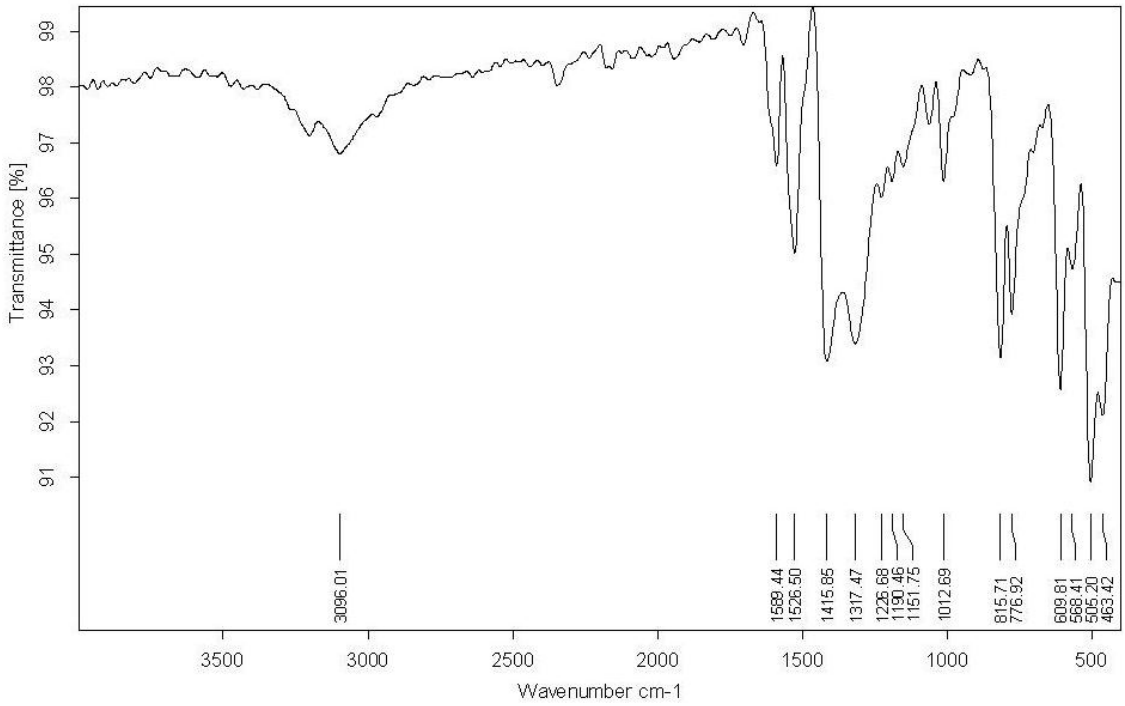

Figure S23: The FT-IR spectrum of compound **4**.

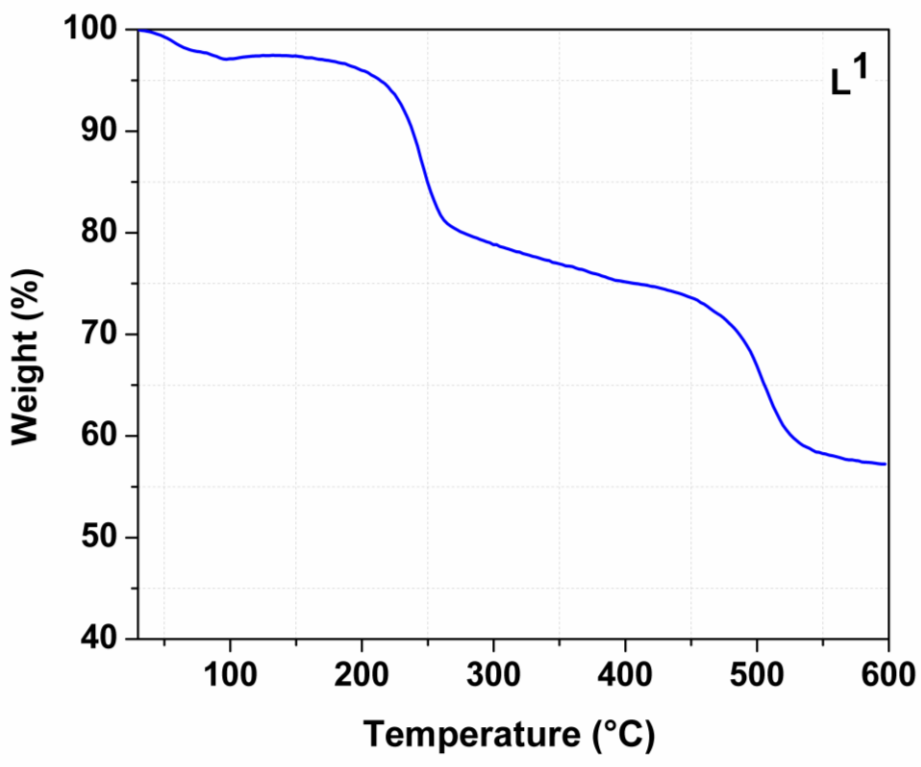

Figure S24: Thermogravimetric analysis of $\mathbf{L^1}$.

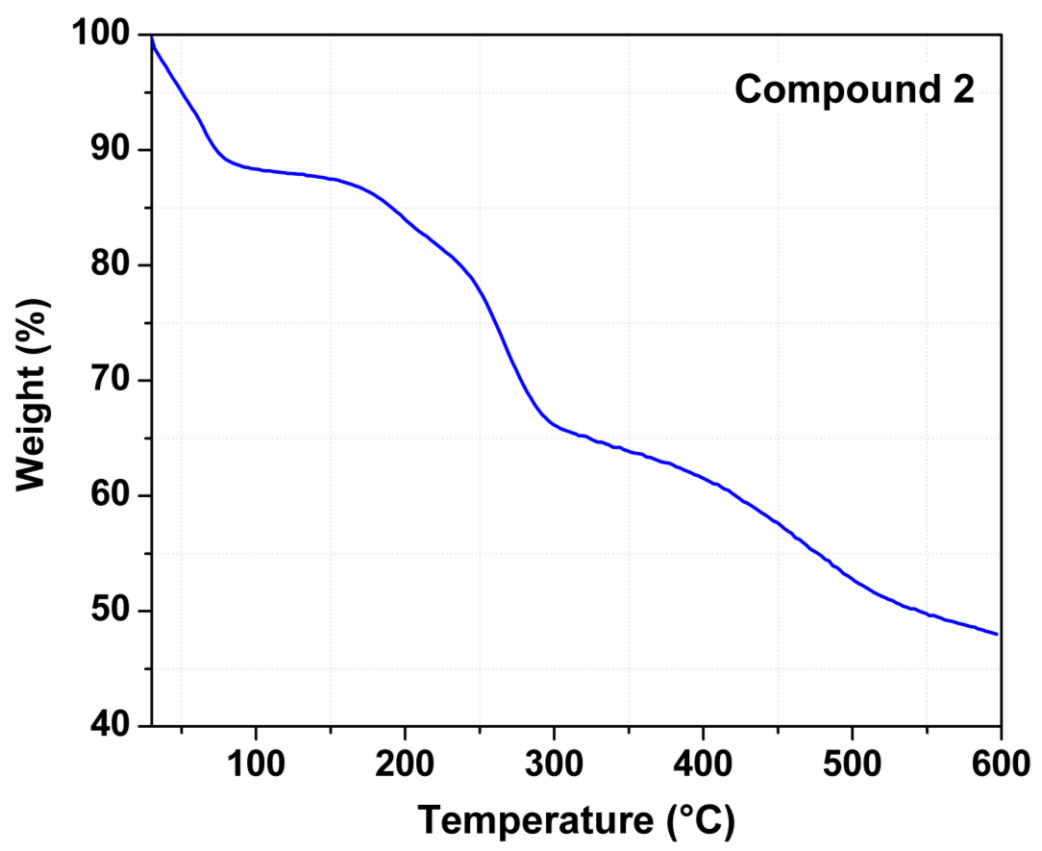

Figure S25: Thermogravimetric analysis of compound **2**.

References.

(1) (a) Meyer, A. S.; Ayers, G. H.; *J. Am. Chem. Soc*. **1957**, *79*, 49-53. (b) Schneider, H. -J. *Principles and Methods in Supramolecular Chemistry*; John Wiley & Sons: New York, **2000**. (c) Connors, K. A. *Binding Constants*; John Wiley & Sons: New York, 1987. (d) Crowley, J. D.; Steele, I. M.; Bosnich B. *Inorg. Chem*. **2005**, *44***,** 2989-2991.

(2) (a) Thordarson, P. *Chem. Soc. Rev.*, **2011**, *40*, 1305-1323. (b) Hibbert, D. B; P. Thordarson, P. *Chem. Commun.*, **2016**, *52*, 12792-12805. (c) Sommer, R. D.; Rheingold, A. L.; Goshe, A. J.; Bosnich. B. *J. Am. Chem. Soc.* **2001**, *123*, 3940-3952.