Supporting Information

Rhenium(I)-based bridgeless double metallocalix[4]arenes

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Contents

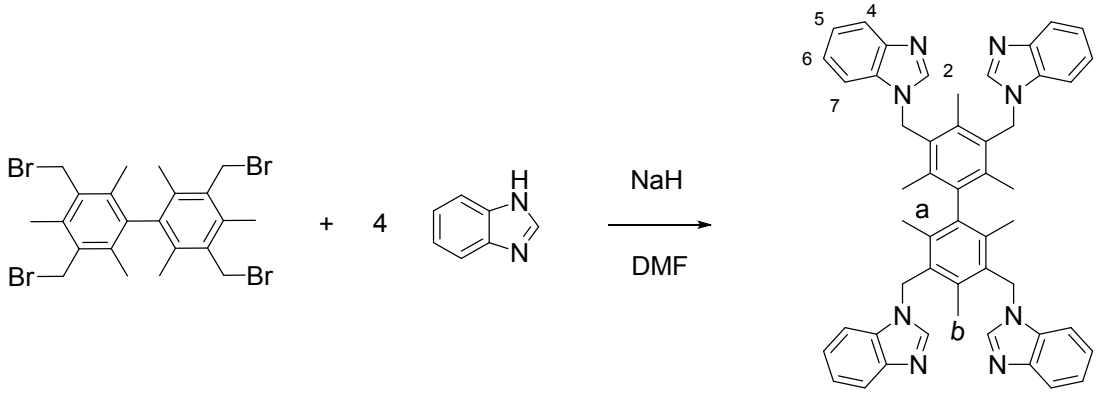
General experimental methods.

All starting materials and products were found to be stable toward moisture and air, and no specific precautions were taken to rigorously excluded air when conventional and solvothermal methods were used. Starting materials such as $Re_2(CO)_{10}$, benzimidazole, H_2-dhnq, H_2-dhaq, mesitylene, DMF, ferric chloride and KOH were procured from commercial sources and used as received. Bimesityl and 3,3',5,5'-tetrakis(bromomethyl)2,2',4,4',6,6'-hexamethylbiphenyl were synthesized following previous reported methods.[S1-S2] FT-IR spectra were recorded on a Perkin-Elmer FTIR-2000 spectrometer. Elemental analyses were performed on a Flash EA series 1112 CHNS analyzer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCEIII 400 instrument. ESI-MS spectra were recorded on Bruker-maXis, microTOF-Q II mass spectrometer. XPS measurements were taken with a custom-built ambient pressure XPS system from Prevac and equipped with a VG Scienta SAX 100 emission controller monochromator using an Al Kα anode (1486.6 eV) in transmission lens mode. [S3-S4] The photoelectrons are energy analyzed using VG Scienta's R3000 differentially pumped analyzer. The electronic absorption spectra were recorded on a Cary 100 Bio, Varian spectrophotometer at room temperature. The emission spectra were recorded on a Fluoromax-4, Horiba Jobin Yvon Fluorescence Spectrophotometer at room temperature.

Intensity data of suitably sized crystals of **1** and **2** were collected on an Rigaku Saturn 724+ CCD diffractometer for unit cell determination and three dimensional intensity data collection. Data integration, indexing and absorption correction using Crystal clear followed by structure solution using the programs in WinGX module.[S5a] The structures were solved by direct methods using SIR 92,[S5b] which revealed the atomic positions, and refined using the SHELX-97 program package[S5c] and SHELXL-97 (within the WinGX program package).[S5d-S5e] Non-hydrogen atoms were refined anisotropically. The detailed crystallographic data's of **1** are given in ESI (Table S1).

Synthesis of L′

A mixture of benzimidazole (388 mg, 3.28 mmol) and NaH (157.44 mg, 6.56 mmol) was stirred in dimethylformamide (10 mL) at room temperature for 2 h. The 3,3',5,5'-tetrakis(bromomethyl)-2,2',4,4',6,6'-hexamethylbiphenyl (500.2 mg, 0.82 mmol) was added to the reaction mixture and continuously allowed to stir for 48 h. The reaction mixture was quenched by adding water (200 mL). The white powder was collected by filtration. Yield: 97 % (1206.2 mg, 1.589 mmol). Anal. Calcd. for $C_{50}H_{46}N_8$ (M.wt. 758.95): C, 79.13; H, 6.11; N, 14.76 %. Found: C, 79.21; H, 6.23; N, 14.65; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.76 (s, 4H, H^2), 7.64-7.62 (m, 4H, H^7), 7.46-7.43 (m, 4 H, H^4), 7.19-7.16 (m, 8H, $H^{5,6}$), 5.53 (s, 8H, -CH_2-), 2.21 (s, 6H, CH_3 (b)) and 1.86 (s, 12H, CH_3 (a)). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 143.94, 143.02, 140.1, 137.91, 136.67, 134.46, 131.1, 130.95, 122.76, 122.13, 120.03, 110.89, 44.31 (*C*H_2), 17.04 (*C*H_3) and 16.2 (*C*H_3). ESI-MS: $[L'+H]^+$ for 759.3891.



References

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(b) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.,* 1994, **27**, 435.

(c) G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

(d) G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112.

(e) L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837.

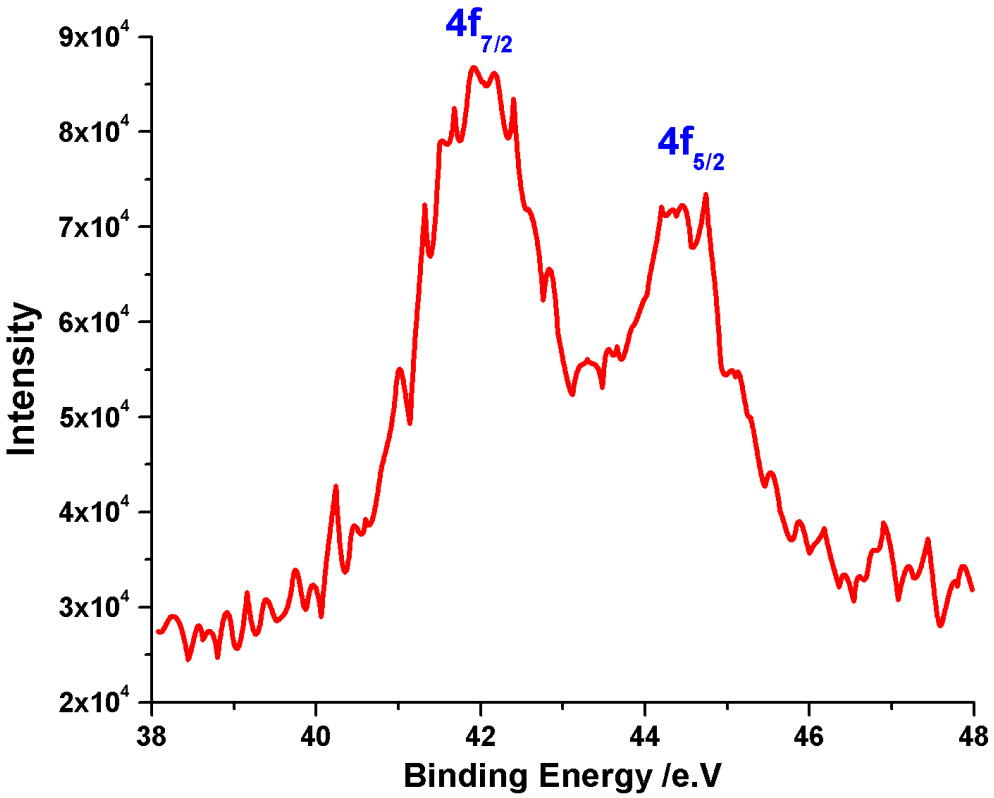


Fig. S1. Re(4f) X-ray photoelectron spectrum of **1** showing $4f_{5/2}$ and $4f_{7/2}$.

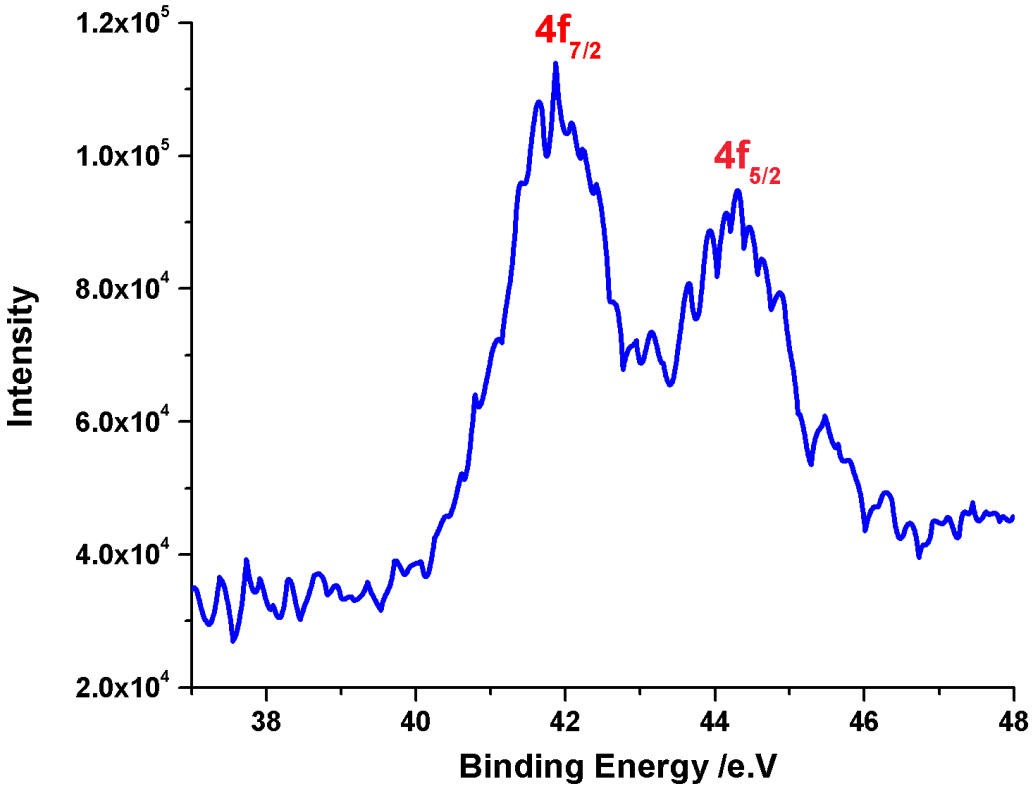


Fig. S2. Re(4f) X-ray photoelectron spectrum of **2** showing $4f_{5/2}$ and $4f_{7/2}$.

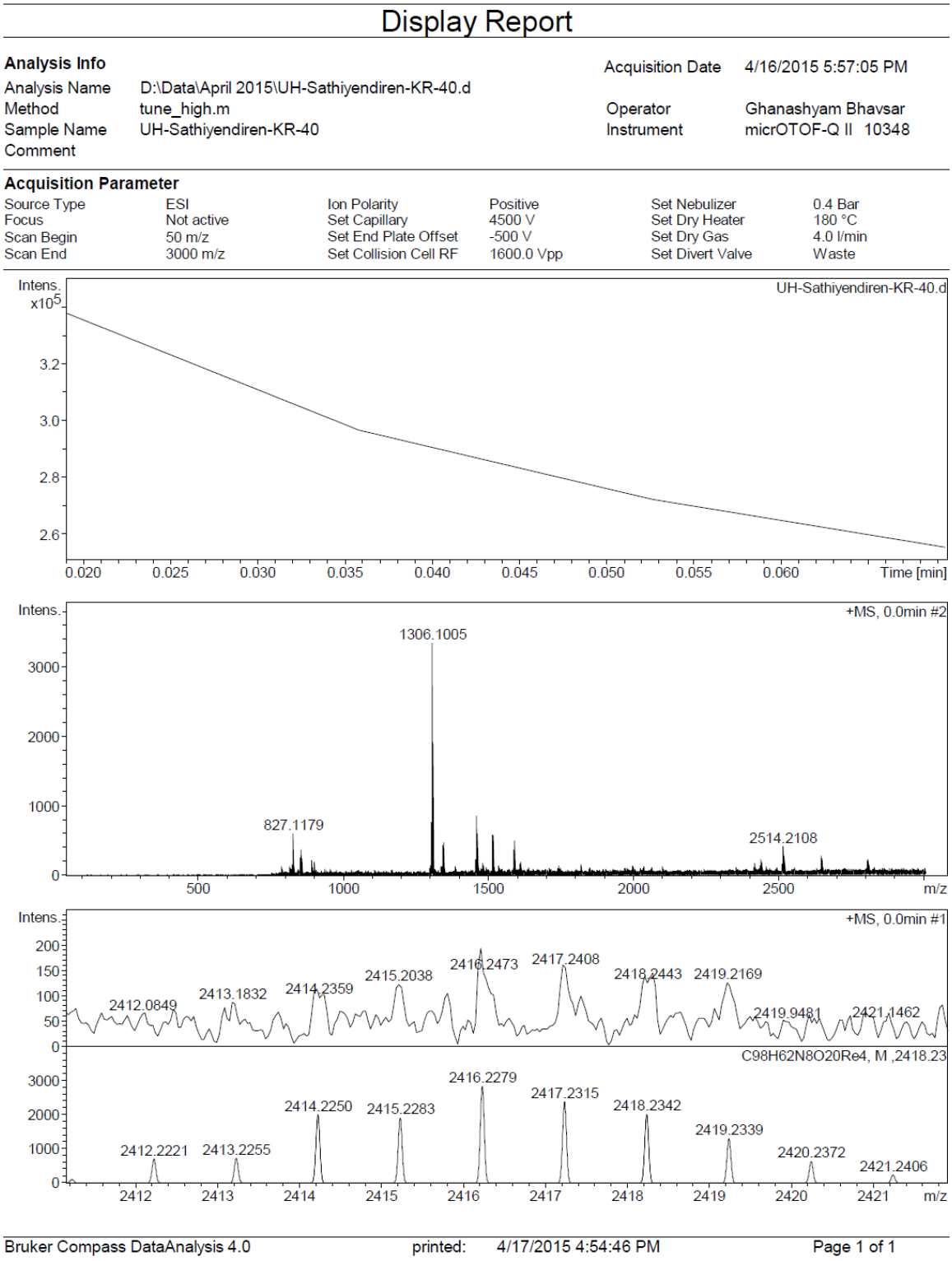


Fig. S3. Top: ESI-MS spectrum of **1** in positive ion mode. Bottom: Experimental (top) and calculated (bottom) ESI-MS spectrum of [**1**]$^{+}$.

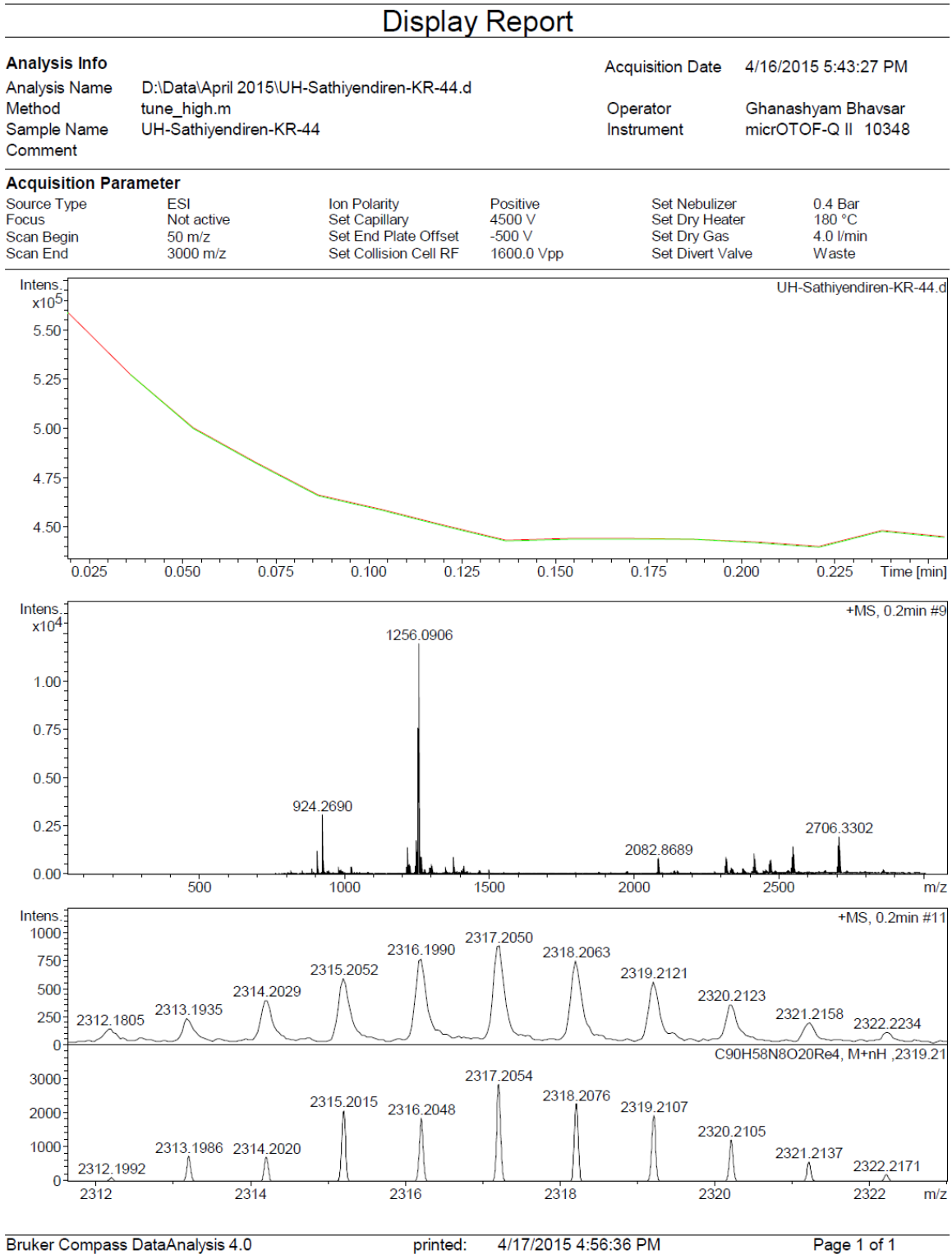


Fig. S4. Top: ESI-MS spectrum of **2** in positive ion mode. Bottom: Experimental (top) and calculated (bottom) ESI-MS spectrum of [**2**+H]$^{+}$.

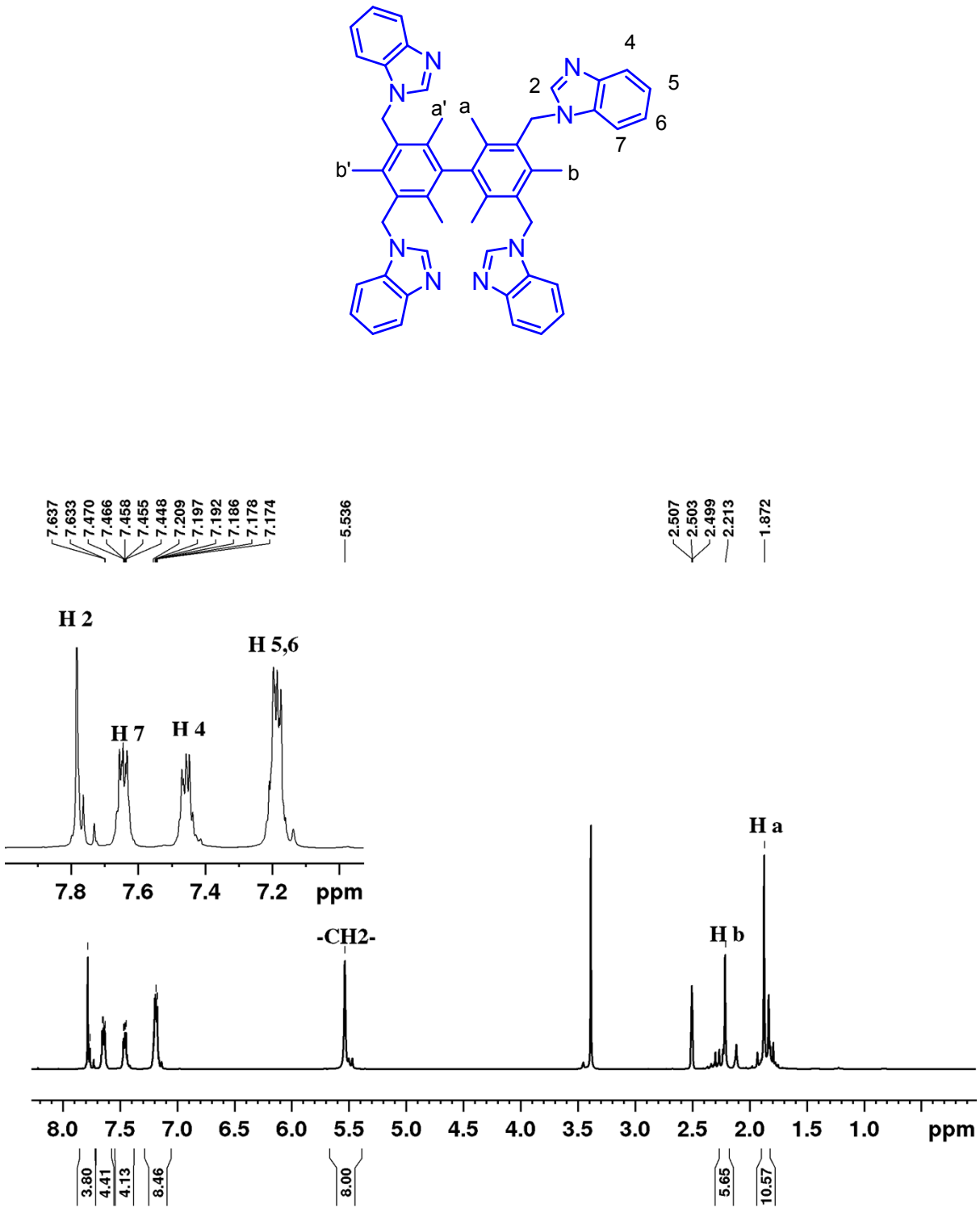
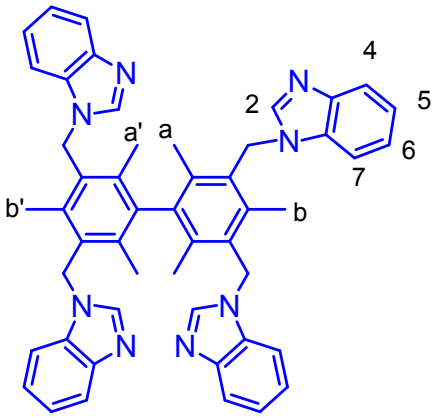


Fig. S5. ^{1}H NMR spectrum of L′ in d_6-DMSO.



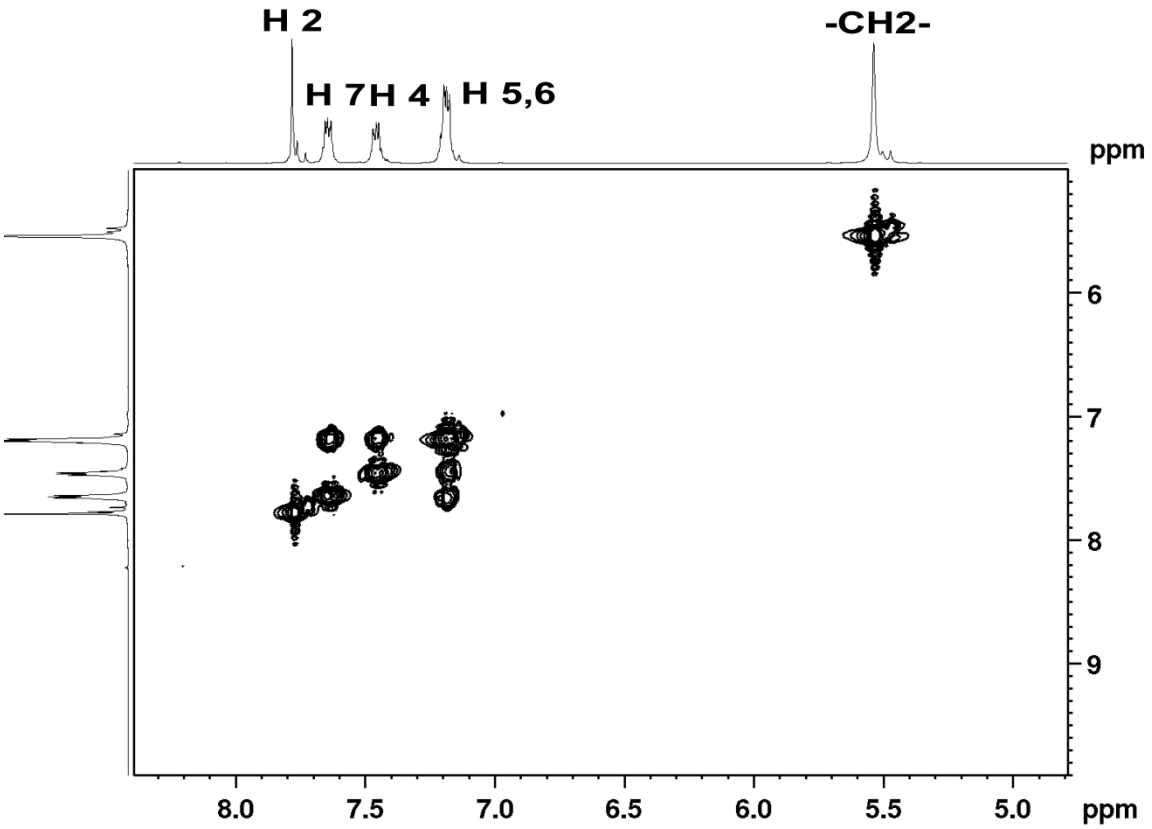


Fig. S6. Partial $^{1}H-^{1}H$ COSY NMR spectrum of the L′ in d_6-DMSO.

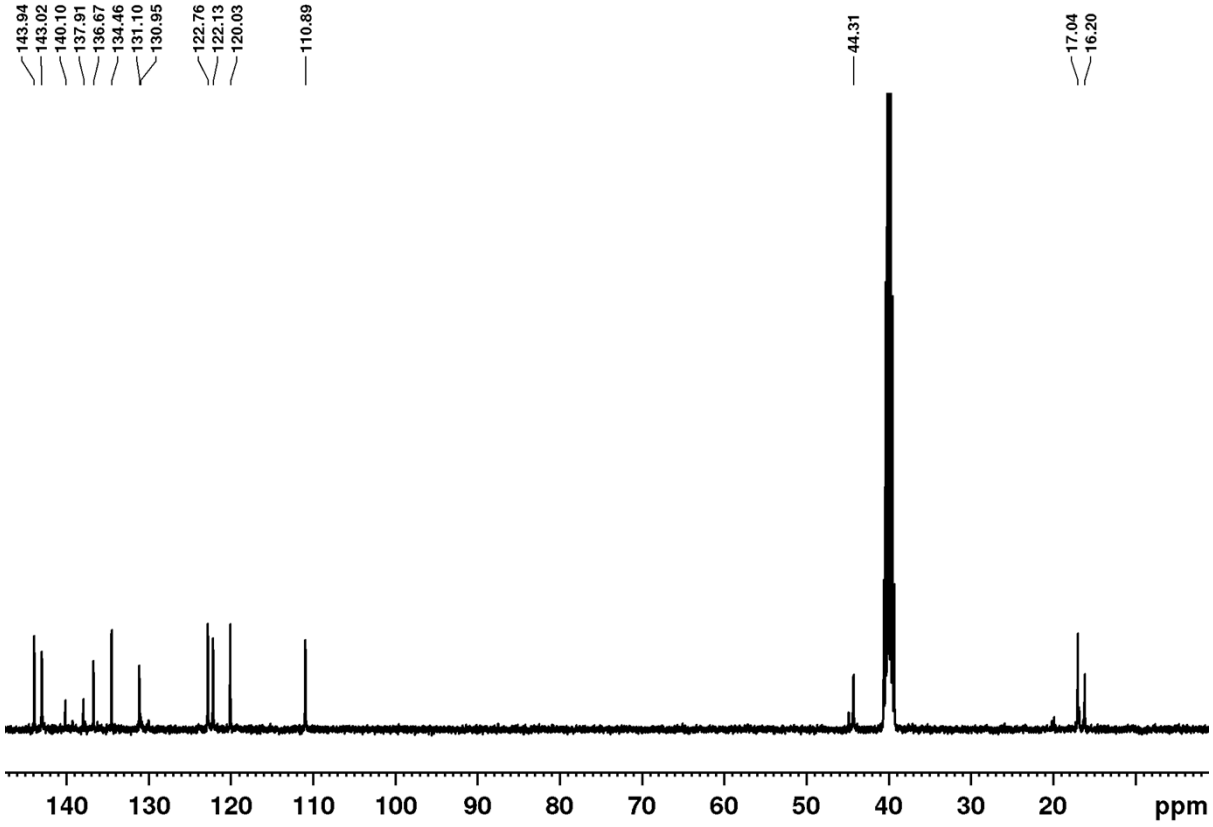


Fig. S7. ^{13}C NMR spectrum of L′ in d_6-DMSO.

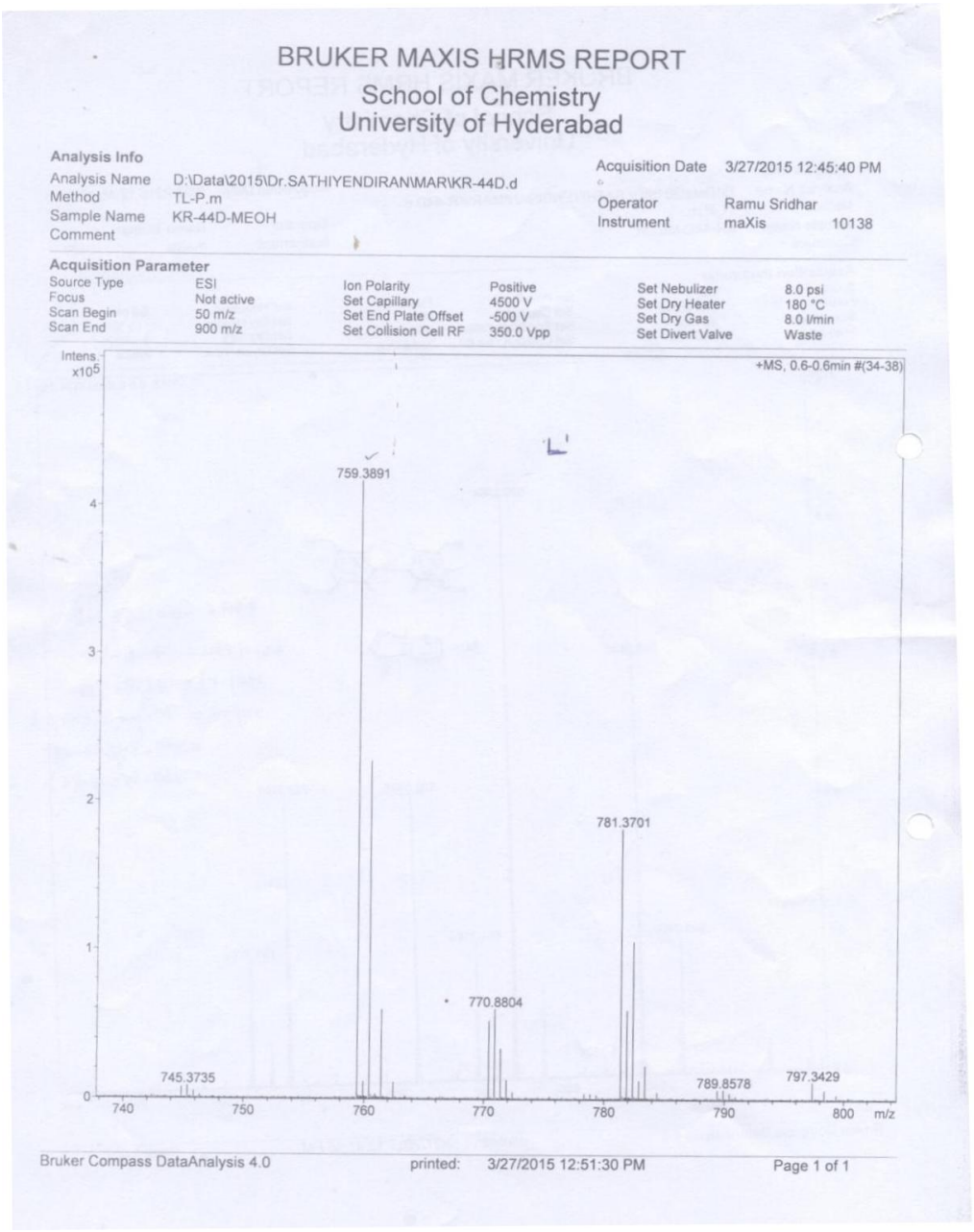


Fig. S8. ESI-MS spectrum of L′ in positive ion mode.

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	$C_{98}\ H_{62}\ N_8 O_{20}\ Re_4$	
Formula weight	2416.36	
Temperature	150(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 19.541(8) Å	α= 90°.
	b = 23.250(9) Å	β= 106.08(2)°.
	c = 25.627(9) Å	γ = 90°.
Volume	11188(7) $Å^3$	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	4.375 mm^{-1}	
F(000)	4664	
Crystal size	0.14 x 0.06 x 0.04 mm^3	
Theta range for data collection	2.67 to 25.00°.	
Index ranges	-23<=h<=22, -17<=k<=27, -30<=l<=30	
Reflections collected	41409	
Independent reflections	9808 [R(int) = 0.0398]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8444 and 0.5794	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9808 / 0 / 587	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.0933	
R indices (all data)	R1 = 0.0530, wR2 = 0.0966	
Largest diff. peak and hole	1.873 and -1.704 e.$Å^{-3}$	

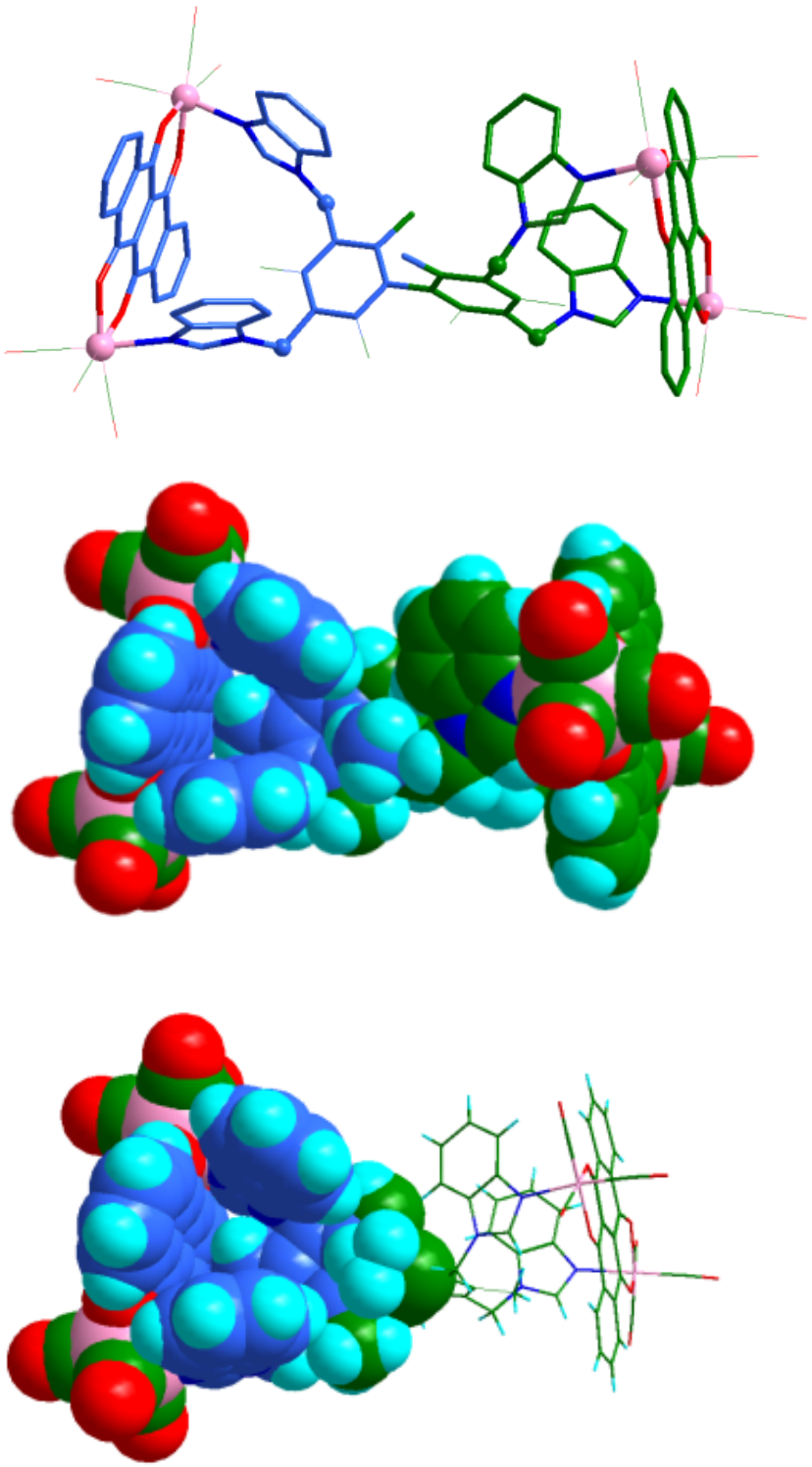


Fig. S9. Top: Molecular structure of **1** showing two metallocalix[4]arenes frameworks (C atoms of the each metallocalix[4]arenes are shown in different colour, CO, and four CH_3 shown as thin stick and H atoms are removed). Middle: Space-filling representation of **1**. Bottom: One metallocavitand is shown in Space-filling view. Light blue = green = C, turquoise = H, blue = N, red = O, and rose = Re.

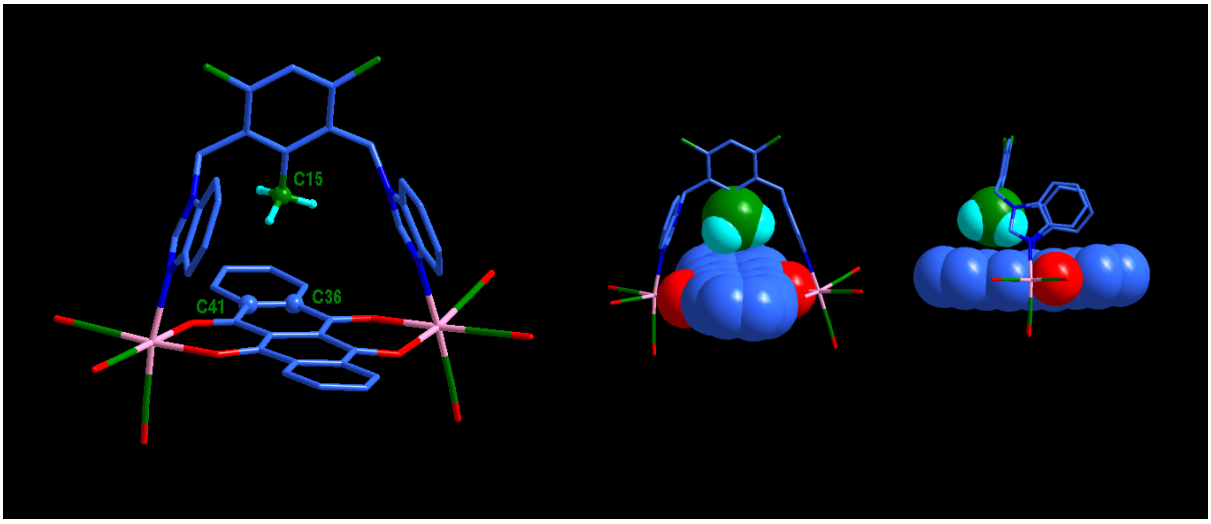


Fig. S10. Compound **1** shows intramolecular non-covalent interactions ($CH_3 \cdots \pi_{dhnq}$ units).

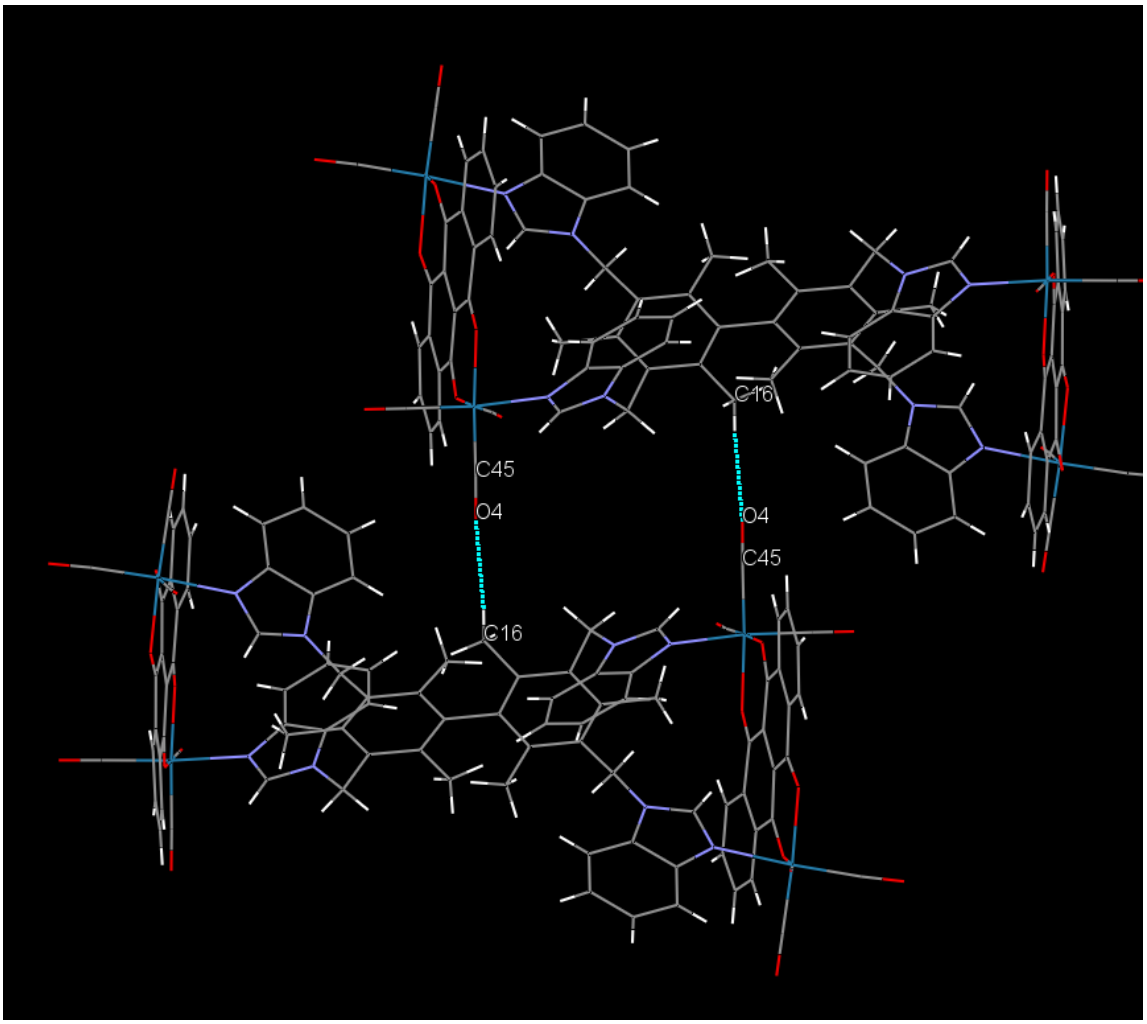


Fig. S11. Two adjacent molecules of **1** showing the nonclassical hydrogen bonding interactions.

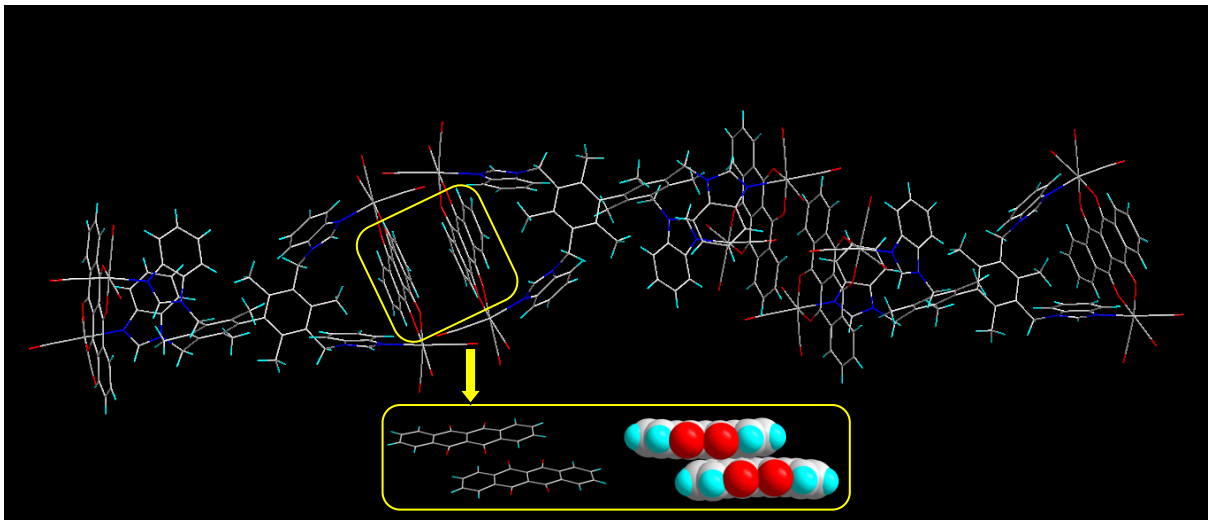


Fig. S12. Partial packing diagram of **1** shows a one-dimensional sheet constructed by π···π stacking interactions. Yellow box indicates the π···π stacking interactions between the dhnq units.

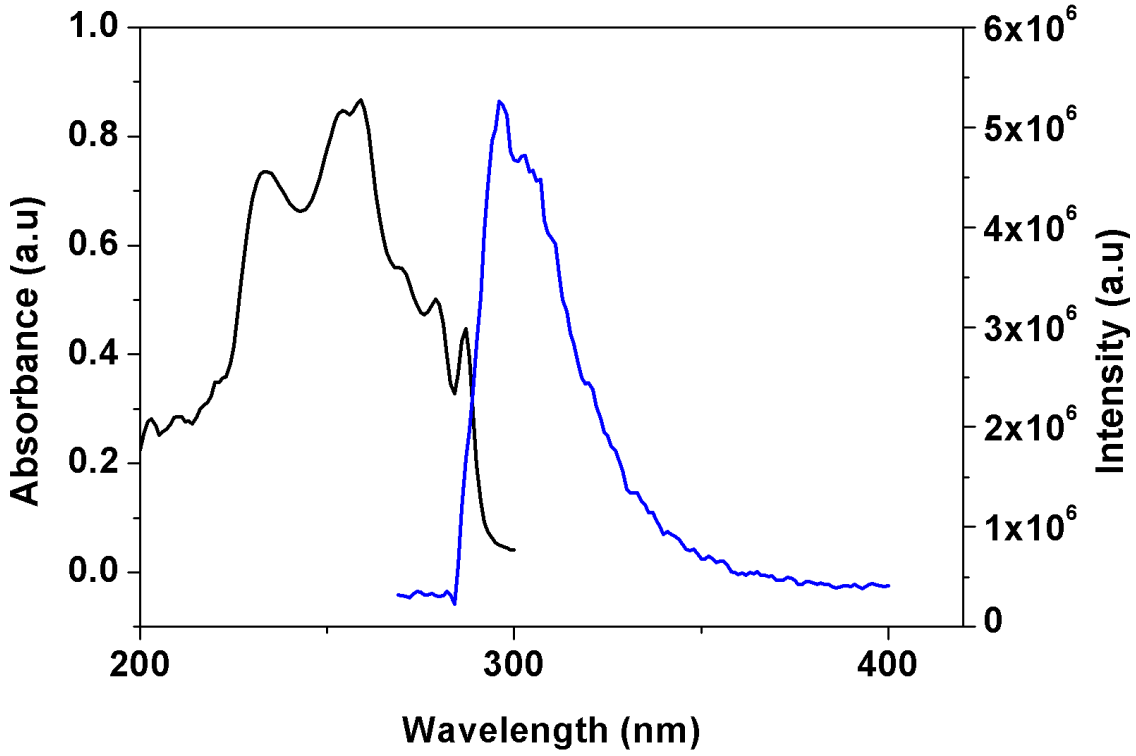


Fig. S13. UV-Vis and emission spectra of L′ in THF.

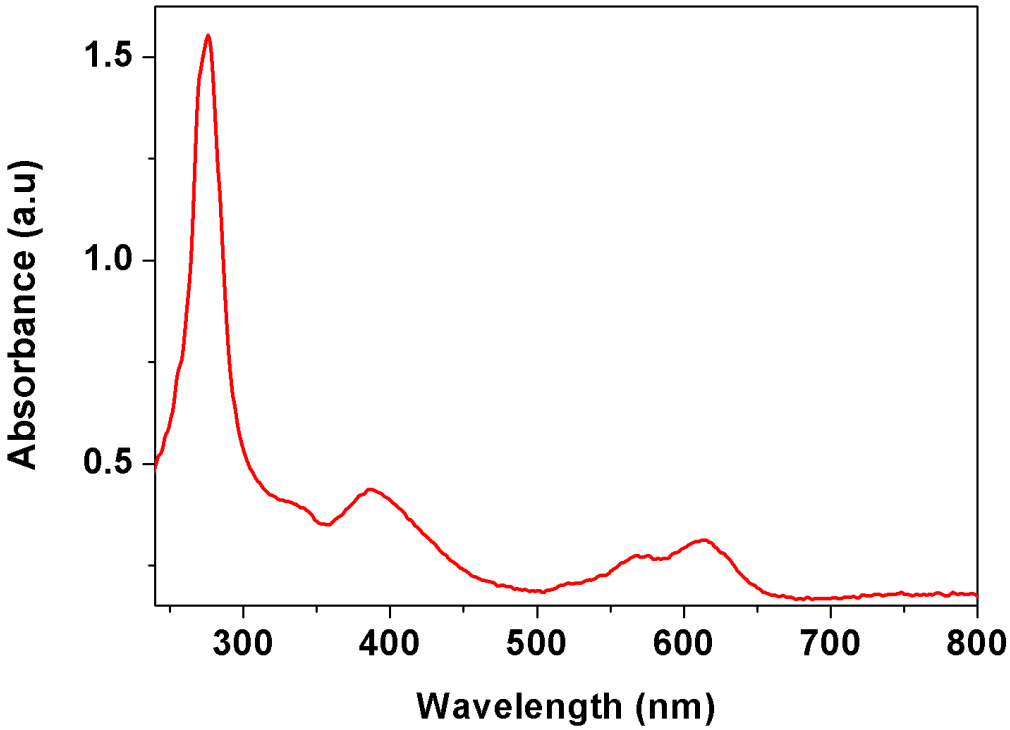


Fig. S14. UV-Vis spectrum of **1** in DMF.

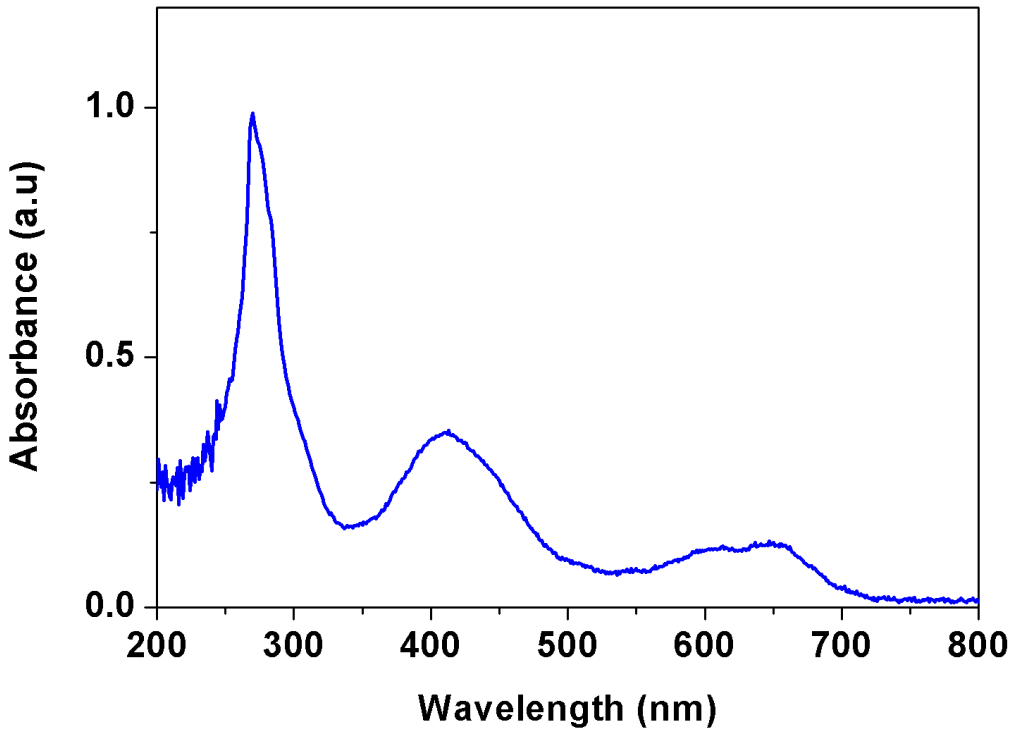


Fig. S15. UV-Vis spectrum of **2** in DMF.

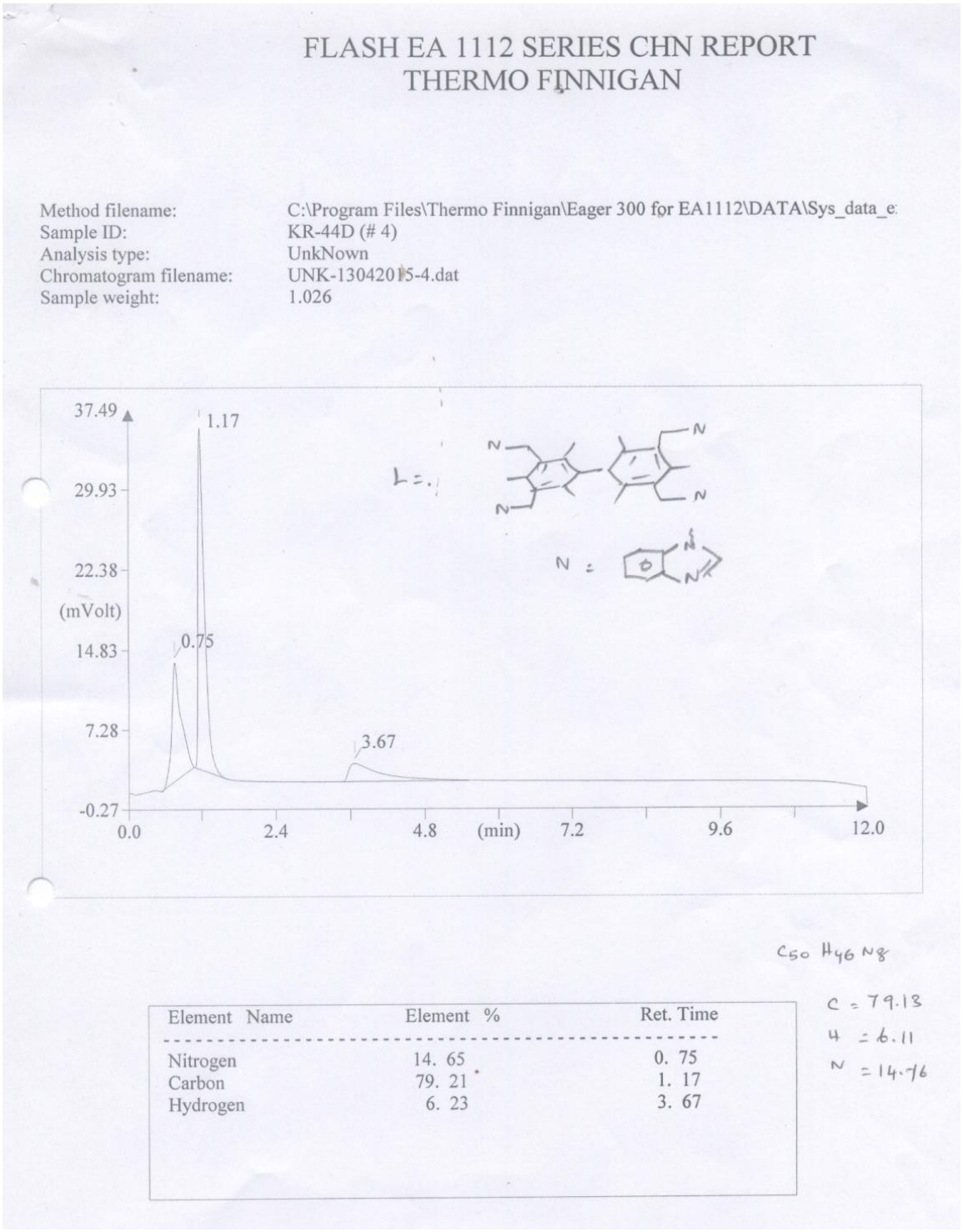


Fig. S16. Copy of elemental analysis data for L′.

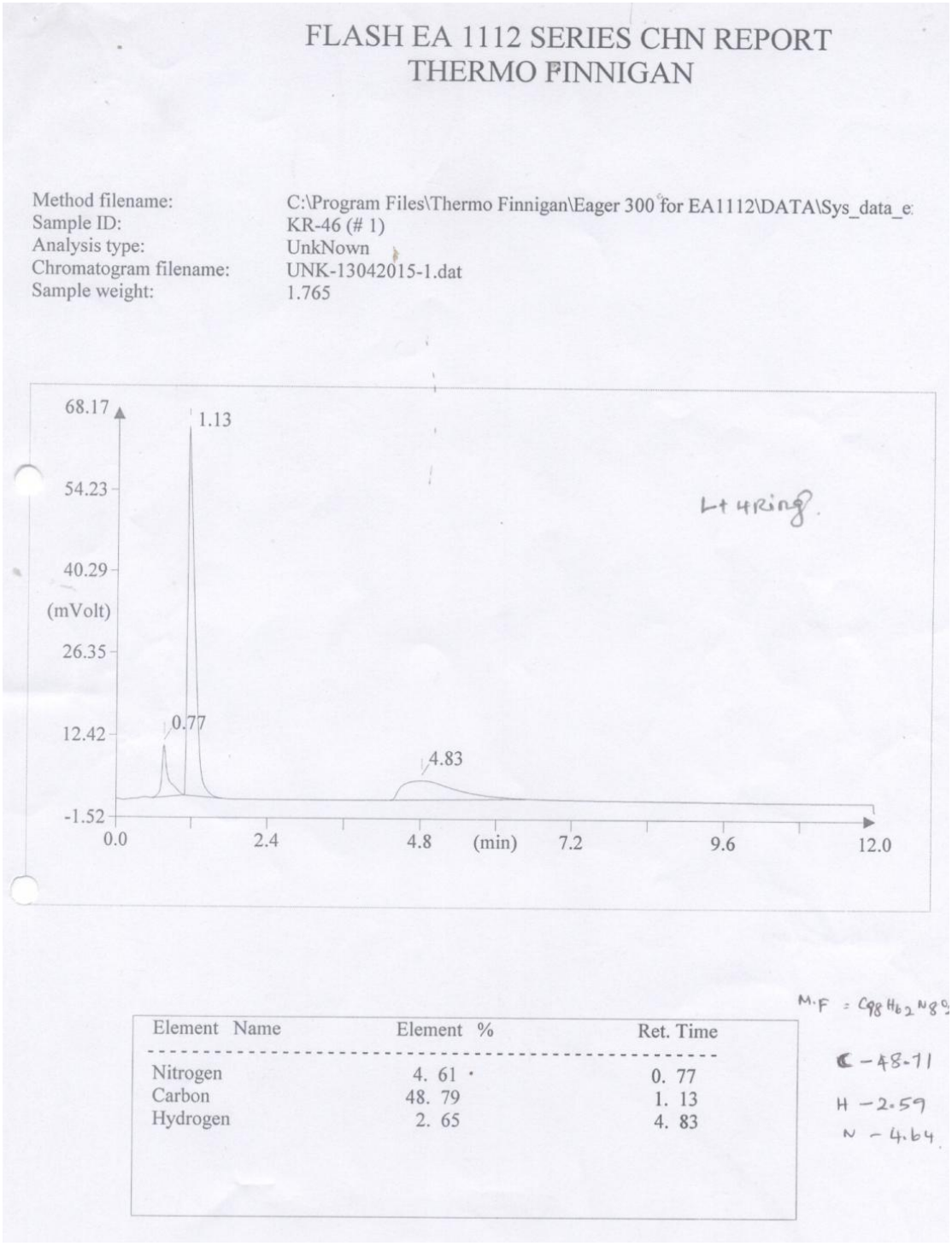


Fig. S17. Copy of elemental analysis data for **1**.

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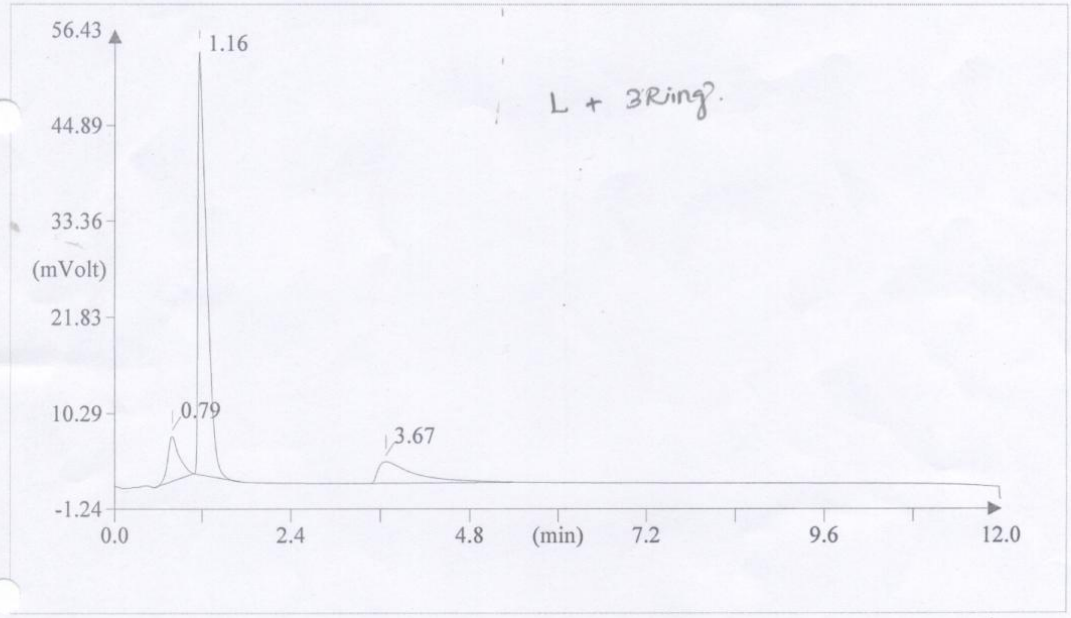

M.F = $C_{90}H_{58}N_8O_{20}Re_4$

Element Name	Element %	Ret. Time
Nitrogen	4. 72	0. 79
Carbon	46. 53	1. 16
Hydrogen	2. 48	3. 67

C - 46.67
H - 2.52
N - 4.84

Fig. S18. Copy of elemental analysis data for **2**.