Supporting Information

Coordination-driven self-assembly of iridium-cornered prismatic cage and encapsulation of three hetero guests in its large cavity

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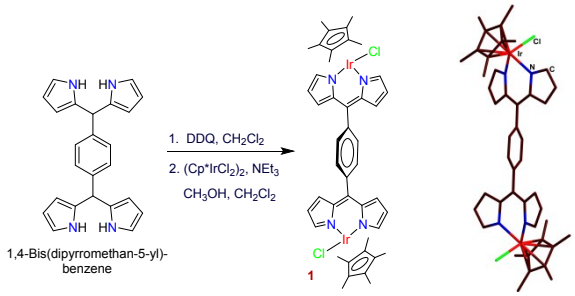
1. Materials and methods

2,4,6-tris(pyridin-4-yl)-1,3,5-triazine(**L**),[S1] 1,4-Bis(dipyrromethan-5-yl)benzene[S2] and N,N'-dimethyl-1,4,5,8-naphthalenetetracarboxylicdiimide(**G_2**)[S3] were synthesized following the reported procedures by standard Schlenk technique. All other reagents were commercially available (Sigma-Aldrich, TCI Korea, Alfa Aesar) and used as received. The solvents were dried and distilled according to the standard literature procedures. The ^{1}H, ^{13}C NMR, ^{1}H-^{1}H ROESY NMR and DOSY NMR spectra were recorded on a Bruker 300 MHz, 600 MHz and 800 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization (ESI) with the MassLynx software suite. Elemental analyses were performed using an Elemental GmbH Vario EL-3 instrument. Absorption spectra were recorded using a CARY 100 Conc UV-Visible spectrophotometer.

2. 1 Synthesis of [(η^5-C_5Me_5)IrCl(bdpmb)] (1)



Scheme 1S. Synthesis and X-ray structure of 1

The solution of 1,4-Bis(dipyrromethan-5-yl)benzene (bdpmb) (72.2 mg, 0.2 mmol) in CH_2Cl_2 (30 mL) was cooled using ice bath. To This solution, DDQ (50.0 mg, 0.22 mmol) dissolved in tuluene (20 mL) was added dropwise with stirring over a period of 10 min and completion of the reaction was confirmed by TLC. After two hour the solvent was removed using rotavapour. The remaining red residue was dissolved in CH_2Cl_2/MeOH (40 mL; 1:1 v/v) and transferred to another two necked round bottom flask discarding the insolubles if any. Triethylamine (0.5 mL) and dimeric iridium complex [{Cp*Ir(μ-Cl)Cl}$_2$] (159.3 mg, 0.20 mmol) were added successively with continuous stirring at rt. After 4 h the solvent was removed using rotavapour and the resulting residue was purified by flash column chromatography (SiO2, CH_2Cl_2 with 2% MeOH) to afford complex 2 as a red solid. Yield: 112.8 mg (52%). Mp: 197-200°C (dec.). Anal. calcd for $C_{44}H_{46}Cl_2Ir_2N_4$: C, 48.65; H, 4.27; N, 5.16. Found: C, 48.27; H, 4.40; N, 5.36. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69(m, 4H, *pyrroleH$_a$*), 7.48 (s, 4H, *PhH$_d$*), 6.60 (dd, *J* = 4.4, 1.1 Hz, 4H, *pyrroleH$_b$*), 6.48 (dd, *J* = 4.4, 1.4 Hz, 4H, *pyrroleH$_c$*), 1.51(S, 30H, *Cp*H$_e$*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.49, 146.35, 137.91, 133.18, 131.62, 129.25, 118.11, 86.57, 8.35. ESI-MS for $C_{44}H_{46}Cl_2Ir_2N_4$: calculated 1051.26 [**1**-Cl]$^{+1}$; observed 1051.41.

2.2 Synthesis of hollow cage 2

The acceptor clip **1** (32.6 mg, 0.03 mmol), ligand **L** (6.3 mg, 0.02 mmol) and AgO_3SCF_3 (15.4 mg, 0.06 mmol) was taken in a reaction vial and 2 mL of MeOH/$MeNO_2$ (1:1) was added. The mixture was stirred at room temperature for 2 h. The reaction mixture was then filtered and concentrated to 0.5 mL under vacuum then diethyl ether was added to precipitate a red solid which was filtered, washed with diethyl ether and dried to furnish **2** as a red crystalline solid. Yield: 43.8 mg (96%). Mp: 208-210°C (dec.). Anal. calcd for

$C_{174}H_{162}F_{18}Ir_6N_{24}O_{18}S_6$: C, 45.78; H, 3.58; N, 7.36; S, 4.21. Found: C, 45.42; H, 3.43; N, 7.14; S, 4.38. ^{1}H NMR (300 MHz, CD_3OD/CD_3NO_2): δ 8.58 (broad s, 24H, $PyH_{\alpha\beta}$), 8.27 (s, 12H, $pyrroleH_b$), 7.54 (s, 6H, PhH_d), 6.84 (s, 6H, PhH_d), 6.75 (dd, J = 4.5, 1.6 Hz, 12H, $pyrroleH_a$), 6.67 (dd, J = 4.5, 1.1 Hz, 12H, $pyrroleH_c$), 1.65 (s, 90H, Cp^*H_e). ^{13}C NMR (75 MHz, CD_3OD/CD_3NO_2) δ 170.77, 153.48, 152.39, 147.78, 145.74, 138.58, 134.52, 133.18, 129.90, 129.67, 126.18, 123.63, 120.58, 90.59, 8.28.

2.3 Synthesis of inclusion complexes [2⊃(G_1)$_2$], [2⊃(G_2)] and [2⊃(G_1•G_2•G_1)]

To a CD_3OD/CD_3NO_2 (1:1, 1 mL) solution of Cage **2** (18 mg, 0.004 mmol) in a reaction vial, electron-rich planner guest coronene (G_1, 3 mol eq.) was added, and the reaction mixture was stirred at room temperature for 5 min. The excess of insoluble guest G_1 was separated using centrifugation, and the ^{1}H-NMR of the clear solution revealed the quantitative formation of the inclusion complex **[2⊃(G_1)$_2$]**. Similarly, inclusion complex **[2⊃(G_2)]** was obtained by the encapsulation of guest, N,N'-dimethyl-1,4,5,8-naphthalenetetracarboxylic diimide (G_2) and the quintuple-stacking structure **[2⊃(G_1•G_2•G_1)]** was formed by the encapsulation of two molecules of **G_1** and one molecule of **G_2** into cage 2.

[2⊃(G_1)$_2$]

^{1}H NMR (300 MHz, CD_3OD/CD_3NO_2): 8.82 (d, J = 5.8 Hz, 12H, PyH_α), 8.47 (s, 12H, $pyrroleH_a$), 7.88 (s, 6H, $outPhH_d$), 7.20 (d, J = 3.9 Hz, 12H, $pyrroleH_b$), 7.12 (d, J = 3.9 Hz, 12H, $pyrroleH_c$), 6.98 (s, 6H, $inPhH_d$), 6.96 (d, J = 5.0 Hz, 12H PyH_β) 6.91 (s, 24H, *coroneneH*), 1.61 (s, 90H, Cp^*H_e)

[2⊃(G_2)]

^{1}H NMR (300 MHz, CD_3OD/CD_3NO_2): δ 8.69 (s, 4H, *NpHg*), 8.57 (m, 24H, $PyH_{\alpha\beta}$), 8.27 (s, 12H, $pyrroleH_b$), 7.56 (s, 6H, $outPhH_d$), 6.86 (s, 6H, $inPhH_d$), 6.75 (dd, J = 4.4, 1.6 Hz, 12H, $pyrroleH_a$), 6.68 (dd, J = 4.4, 0.8 Hz, 12H, $pyrroleH_c$), 3.51 (s, 6H, $N\text{-}methylH_h$), 1.65 (s, 90H, Cp^*H_e).

[2⊃(G_1·G_2·G_1)]

^{1}H NMR (300 MHz, CD_3OD/CD_3ON_2): δ 8.68 (d, J = 6.7 Hz, 12H, PyH_α), 8.43 (s, 12H, $pyrroleH_a$), 8.01 (s, 6H, $outPhH_d$), 7.70 (s, 6H, $inPhH_d$), 7.34 (dd, J = 4.5, 1.1 Hz, 12H, $pyrroleH_c$), 7.24 (dd, J = 4.6, 1.6 Hz, 12H, $pyrroleH_b$), 6.71 (d, J = 6.7Hz, 12H, PyH_β), 4.47 (s, 4H, *NpHg*), 2.02 (s, 1H, $N\text{-}methylH_h$), 1.58 (s, 90H, Cp^*H_e).

2.3 Synthesis of encapsulated cage [2⊃(G_1·G_2·G_1)] direct from ligand L and acceptor clip 1

The encapsulated cage **[2⊃(G_1·G_2·G_1)]** was also synthesized by an identical method described above for the synthesis of hollow cage **2** except that **G_1** (1 mol eq. of **L**) and **G_2** (0.5 mol eq. of **L**) was also added. The quantitative product obtained after workup was identical with **[2⊃(G_1·G_2·G_1)]** synthesized from hollow cage as described above.

3. Crystallographic data collection and refinement of the structures

Single crystal of **1**, **[2⊃(G_2)]** and **[2⊃(G_1•G_2•G_1)]** were coated with paratone-*N* oil and the diffraction data measured at 100 K with synchrotron radiation (λ = 0.61000 Å) on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program[S4] was used for data collection (detector distance is 125 mm, omega scan; Δω = 3º, exposure time is 1 sec per frame) and HKL3000sm (Ver. 703r)[S5] was used for cell refinement, reduction and absorption correction. The crystal structures were solved by the direct method with SHELXTL-XS program and refined by full-matrix least-squares calculations with the SHELXTL-XL (Ver. 2008) program package.[S6]
All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) and 1.5U (C_{methyl}), their coordinates were allowed to ride on their respective

atoms.

For **[2⊃(G$_1$•G$_2$•G$_1$)]** the least-squares refinement of the structural model was performed under displacement parameter restraints such as DANG, DELU, DFIX, FLAT, ISOR, SAME and SIMU. The final refinement was performed with the modification of the structure factors for the electron densities of the unidentified molecules and the disordered solvents using the SQUEEZE option of PLATON.[S7] The largest difference peak and hole were 1.536 and −0.742 e·Å^{-3}, respectively. A summary of crystals and important crystallographic data are given in Table S1.

4. Table S1. X-Ray crystal structure parameters of compounds **1**, **[2⊃(G$_1$)$_2$]** and **[2⊃(G$_2$•G$_1$•G$_2$)]**

Parameters	**1**	**[2⊃(G$_1$)$_2$]**	**[2⊃(G$_1$•G$_2$•G$_1$)]**
Formula	$C_{46}H_{50}Cl_6Ir_2N_4$	$C_{254}H_{218}F_{18}Ir_6N_{24}O_{21}S_6$	$[C_{256}H_{208}Ir_6N_{26}O_4]^{+6}$
mol wt	1256.04	5630.21	4865.81
cryst syst	Triclinic	Monoclinic	Tetragonal
Space group	*P***Error!**	$P2_1/n$	I-42d
a (Å)	7.991(2)	27.189(5)	46.154(7)
b (Å)	9.776(2)	30.491(6)	46.154(7)
c (Å)	15.449(3)	29.069(6)	49.592(10)
α (deg)	100.26(3)	90	90
β (deg)	102.15(3)	100.26(3)	90
γ (deg)	103.55(3)	90	90
V (Å^3)	1113.7(5)	23713(8)	105641(38)
Z	1	4	16
T /K	100	100	100
λ (Å)	0.70000	0.70000	0.61000
ρ_{calcd} (g/cm^3)	1.873	1.577	1.224
μ (mm^{-1})	6.092	3.342	2.062
Goodness of fit	1.093	1.155	0.922
θ range (deg)	2.27-26.0	1.72-25.94	0.52-20.01
total no. of rflns	7504	48385	277146
no. of unique rflns	3838	48385	39030
no. of obsd data($I > 2\sigma(I)$)	3820	41929	23480
R_{int}	0.0179	0.0000	0.1018
$R(F^2 > 2\sigma(F^2))$, $wR(F^2)$[a]	0.0317, 0.0933	0.0781, 0.2826	0.0711, 0.2027
CCDC	1036112	1036113	1036114

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma [w(|F_o^2 - |F_c^2|)^2] / \Sigma|w(F_o^2)^2|\}^{1/2}$

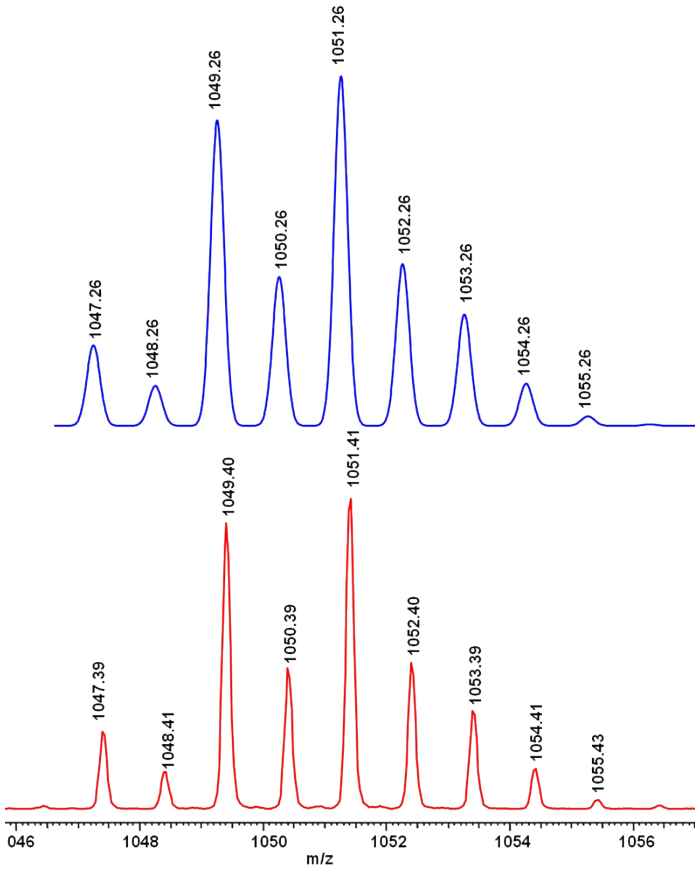


Figure 1S. Calculated (in blue) and experimental (in red) ESI-MS of acceptor clip $[\mathbf{1}]^{+}$

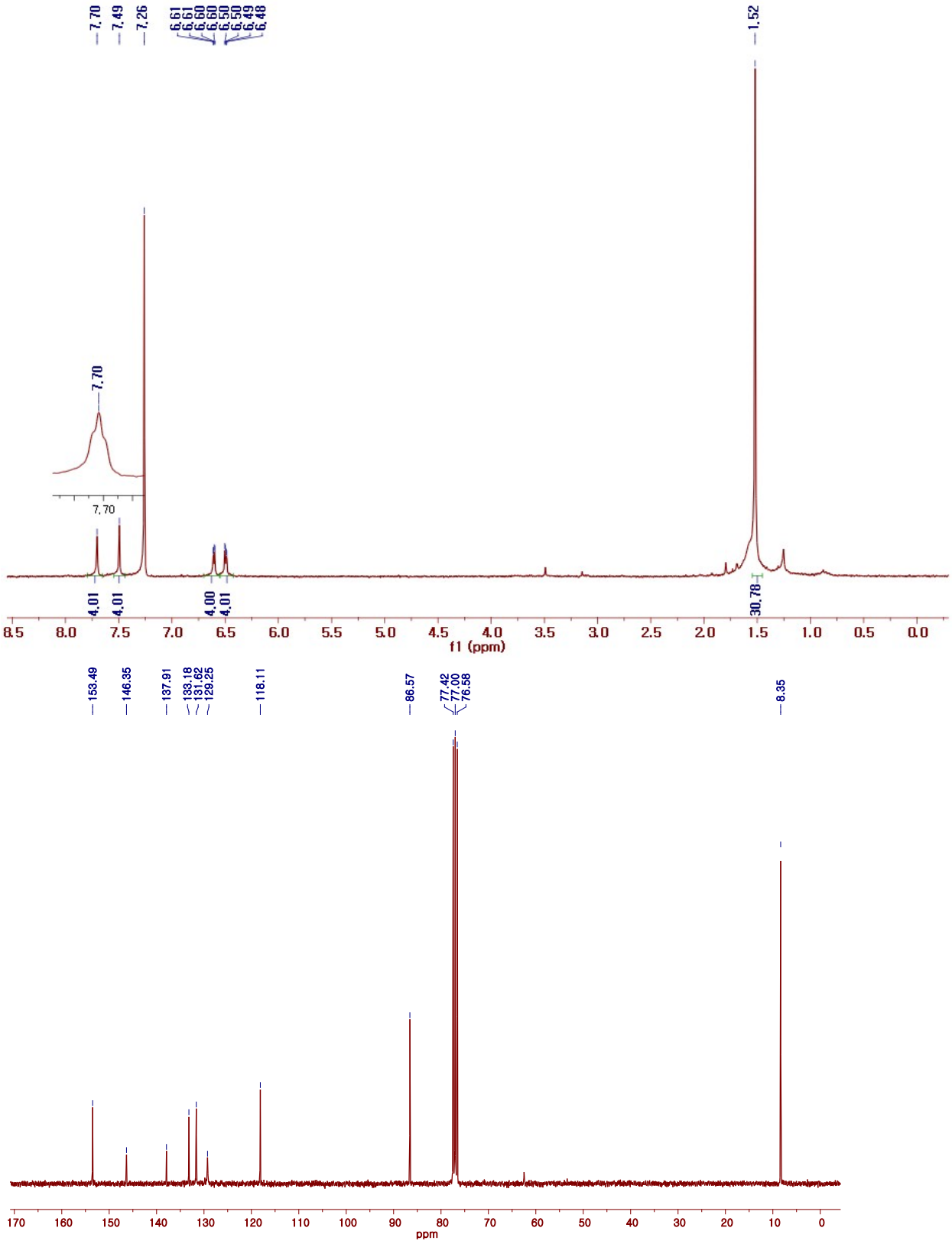


Figure 2S. ^{1}H (top) and ^{13}C (bottom) NMR spectrum of **1** in $CDCl_3$

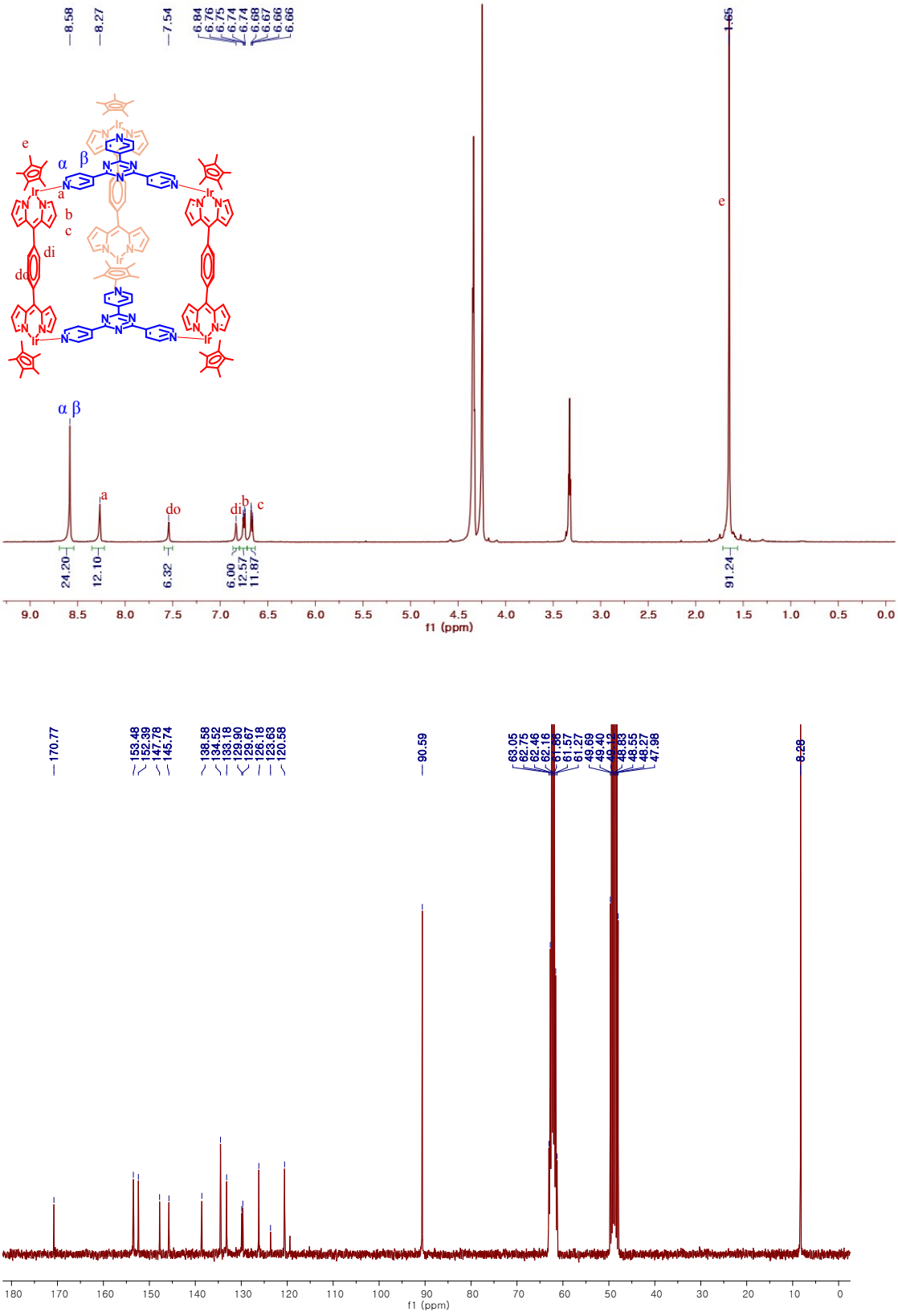


Figure 3S. ^{1}H (top) and ^{13}C (bottom) NMR spectrum of **2** in CD_3OD/CD_3NO_2

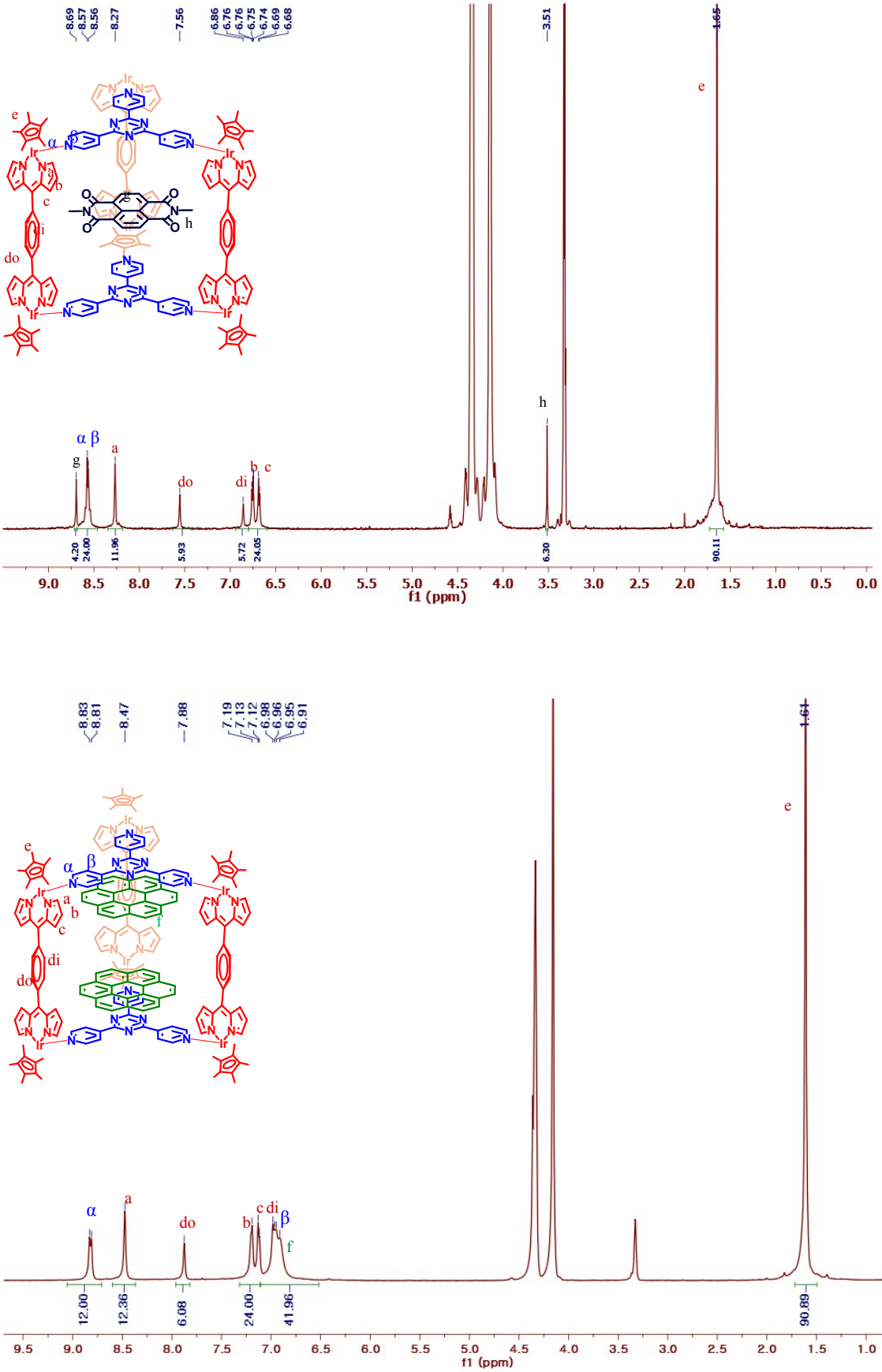


Figure 4S. ^{1}H NMR spectrum of **[2⊃G$_2$]** (top) and **[2⊃(G$_1$)$_2$]** (bottom) in CD_3OD/CD_3NO_2

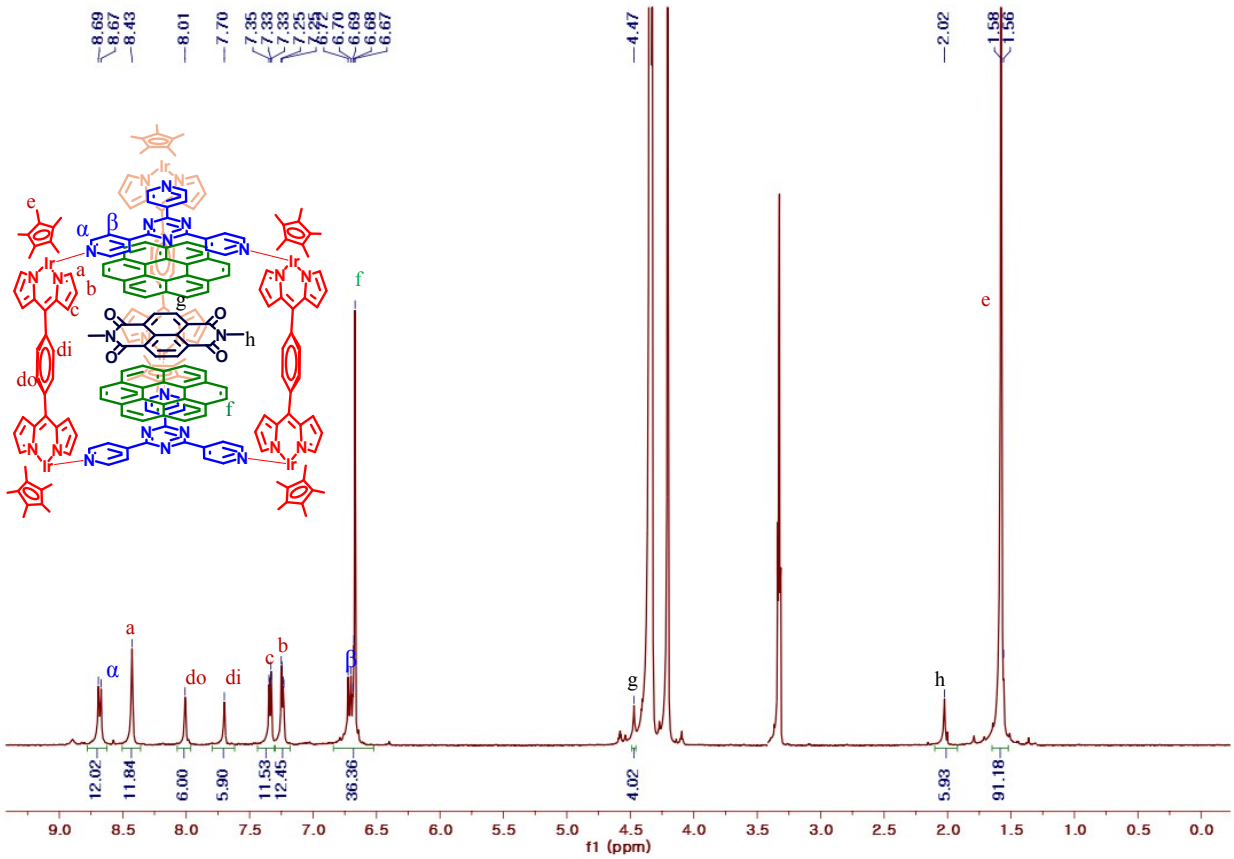


Figure 5S. ^{1}H NMR spectrum of **[2⊃(G$_1$•G$_2$•G$_1$)]** in CD_3OD/CD_3NO_2

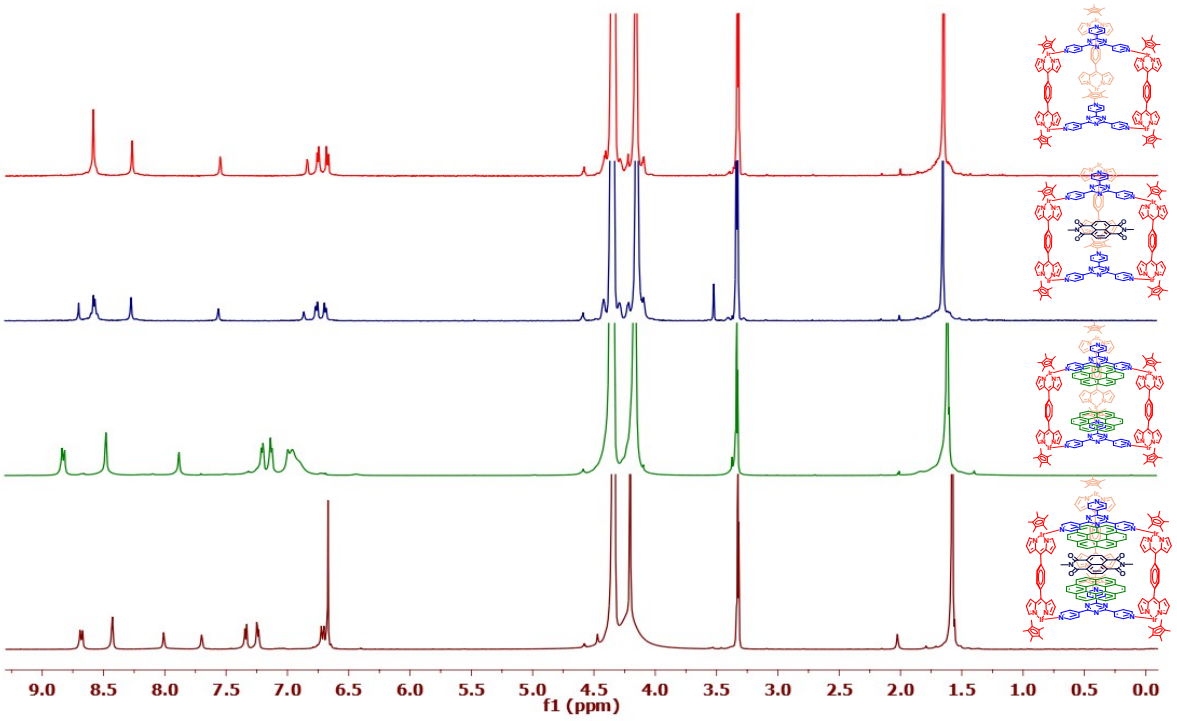


Figure 6S. Comparison of ^{1}H NMR spectra of **2, [2⊃G$_2$], [2⊃(G$_1$)$_2$]** and **[2⊃(G$_1$•G$_2$•G$_1$)]** in CD_3OD/CD_3NO_2

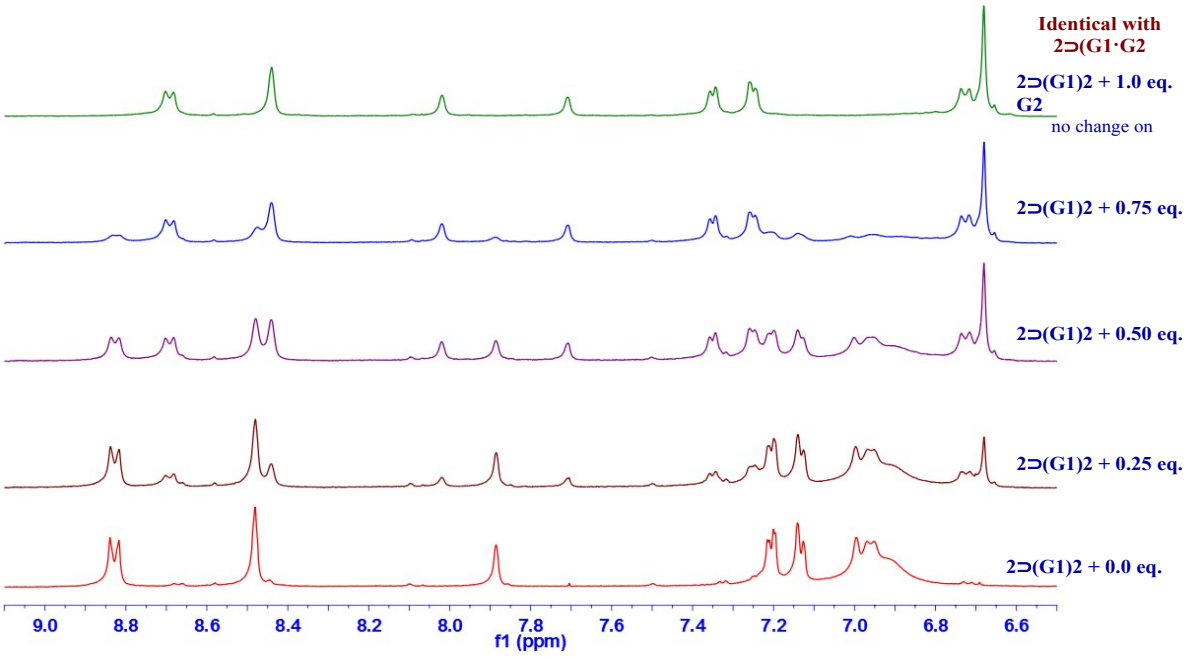


Figure 7S. Transformation of ^{1}H-NMR spectrum of **[2⊃(G1)$_2$]** to the spectrum of **[2⊃(G$_1$•G$_2$•G$_1$)]** upon increasing addition of G$_2$

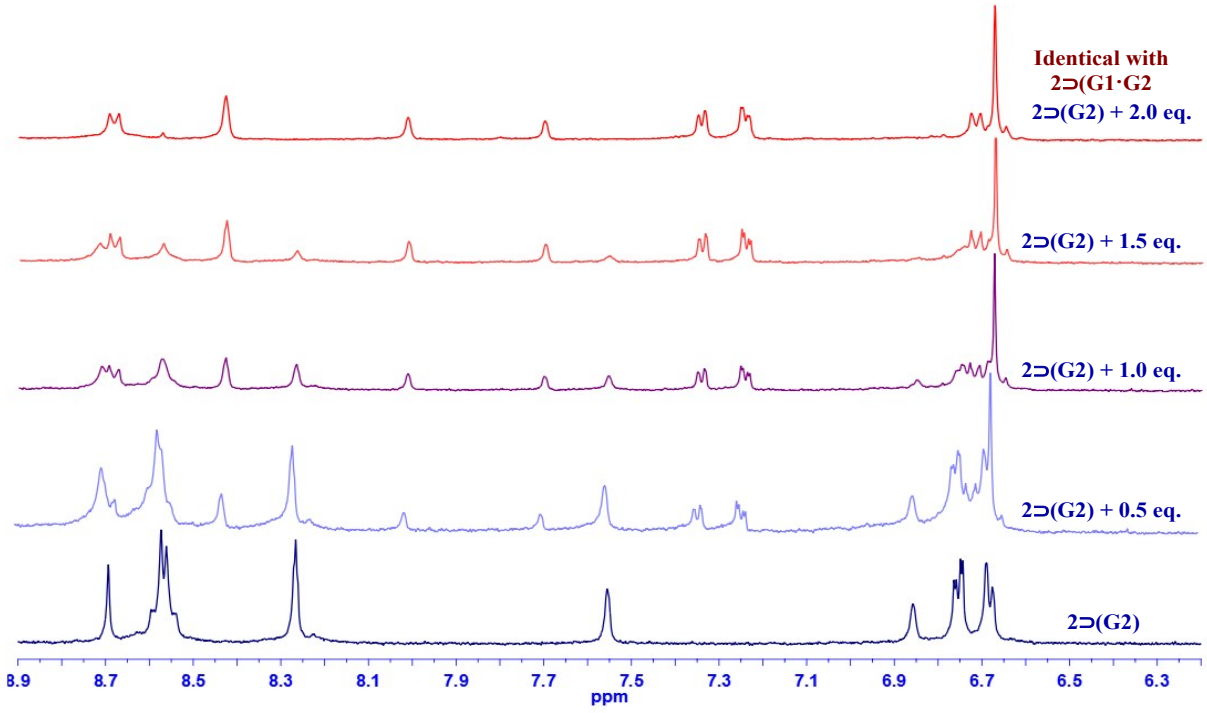


Figure 8S. Transformation of ^{1}H-NMR spectrum of **[2⊃(G$_2$)]** to the spectrum of **[2⊃(G$_1$•G$_2$•G$_1$)]** upon increasing addition of G$_1$

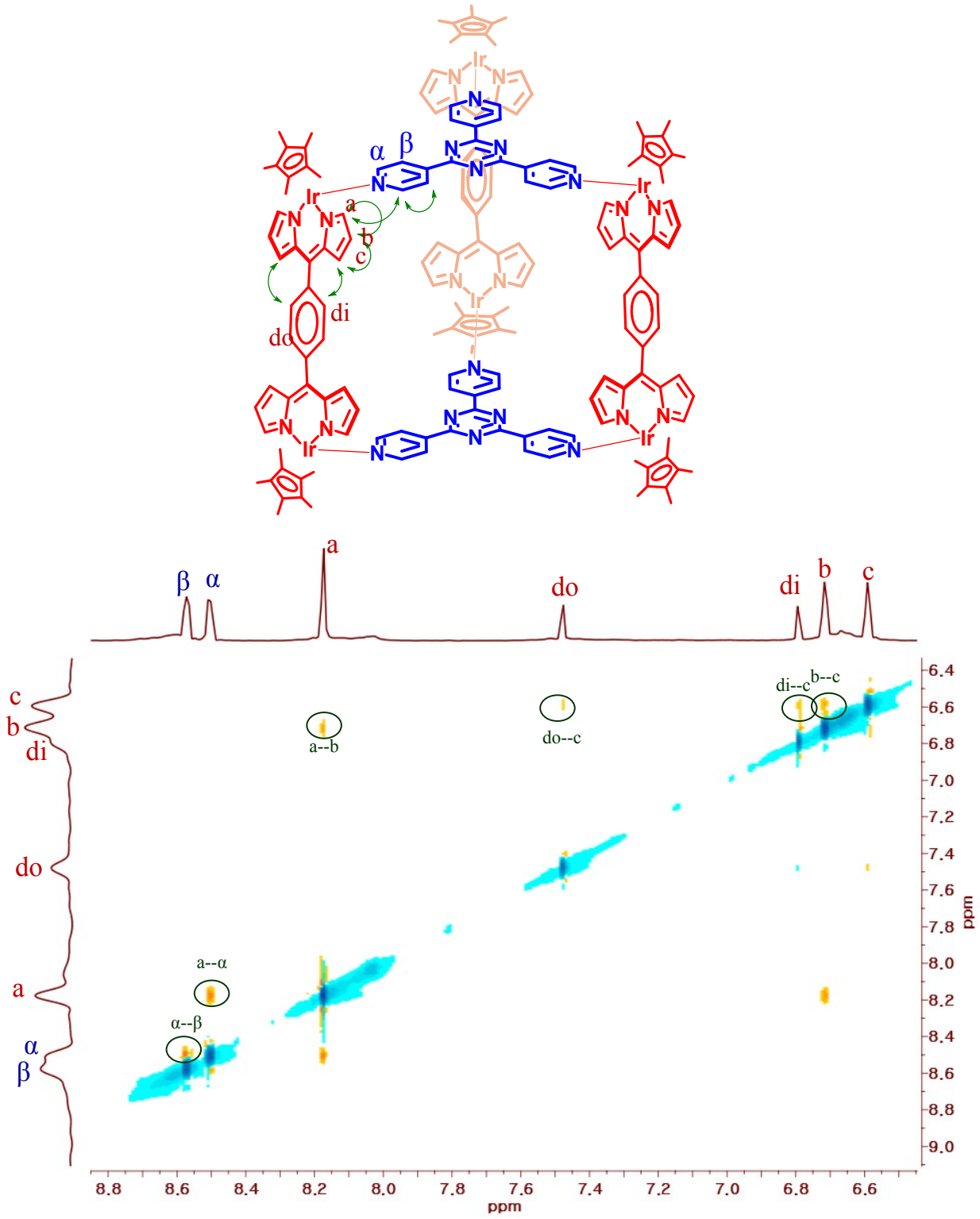


Figure 9S. Partial ^{1}H-^{1}H ROESY NMR spectrum of **2** with coupling interactions highlighted (1:1 CD_3OD/CD_2Cl_2, 298 K, 600 MHz). (Green arrow indicating observed coupling interactions)

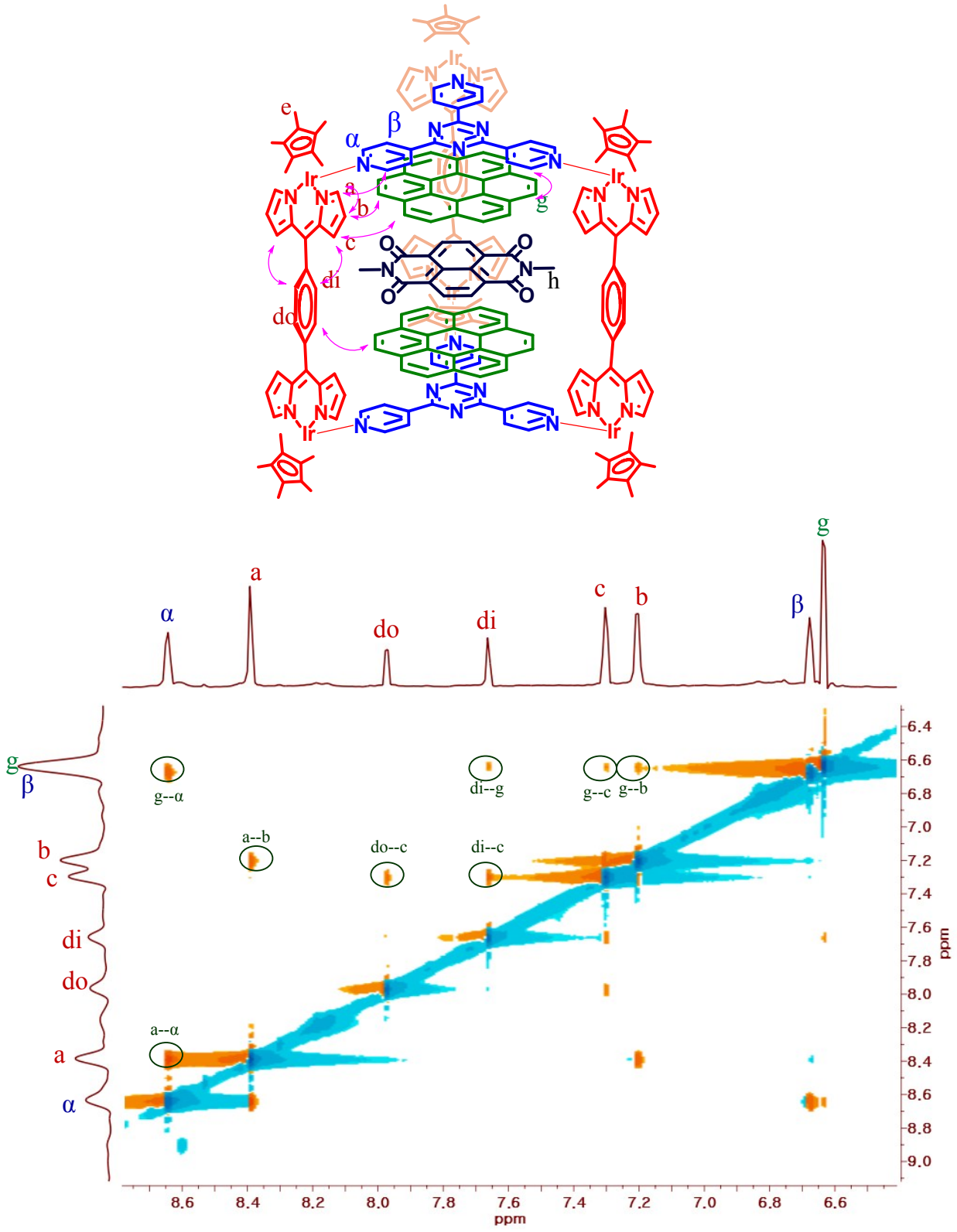


Figure 10S. Partial ^{1}H-^{1}H ROESY NMR spectrum of **[2⊃(G_1•G_2•G_1)]** with coupling interactions highlighted (1:1 CD_3OD/CD_3NO_2, 298 K, 600 MHz). (Pink arrow indicating observed coupling interactions)

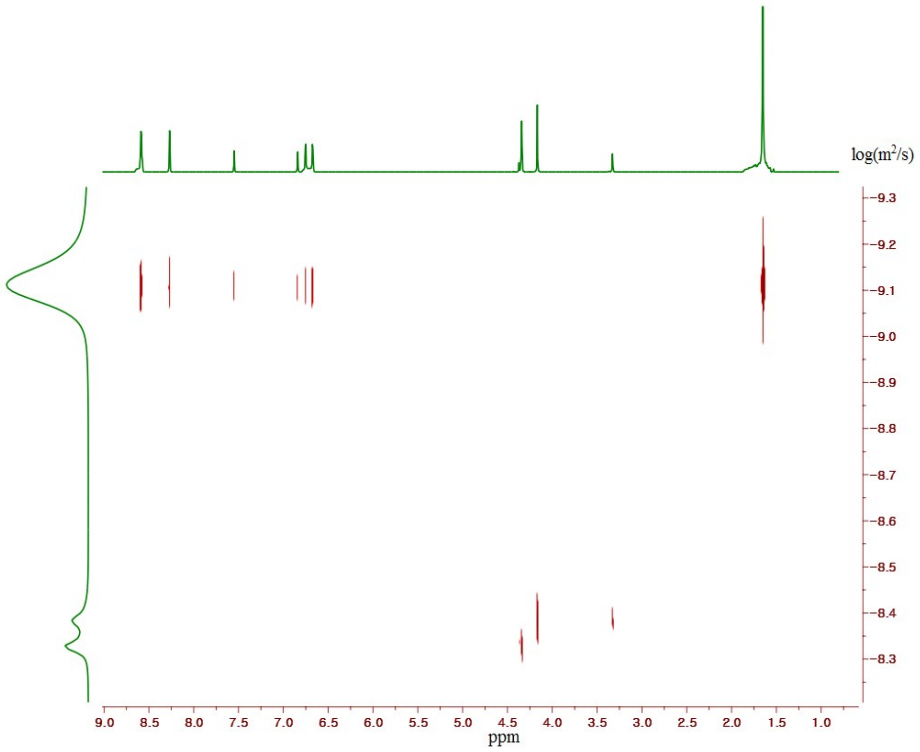


Figure 11S. DOSY NMR spectrum of **2** (1:1 CD_3NO_2/CD_3OD, 298 K, 800 MHz) showing peaks associated with the prismatic cage 2 with diffusion coefficient of $7.93X10^{-10}$ m^2/sec.

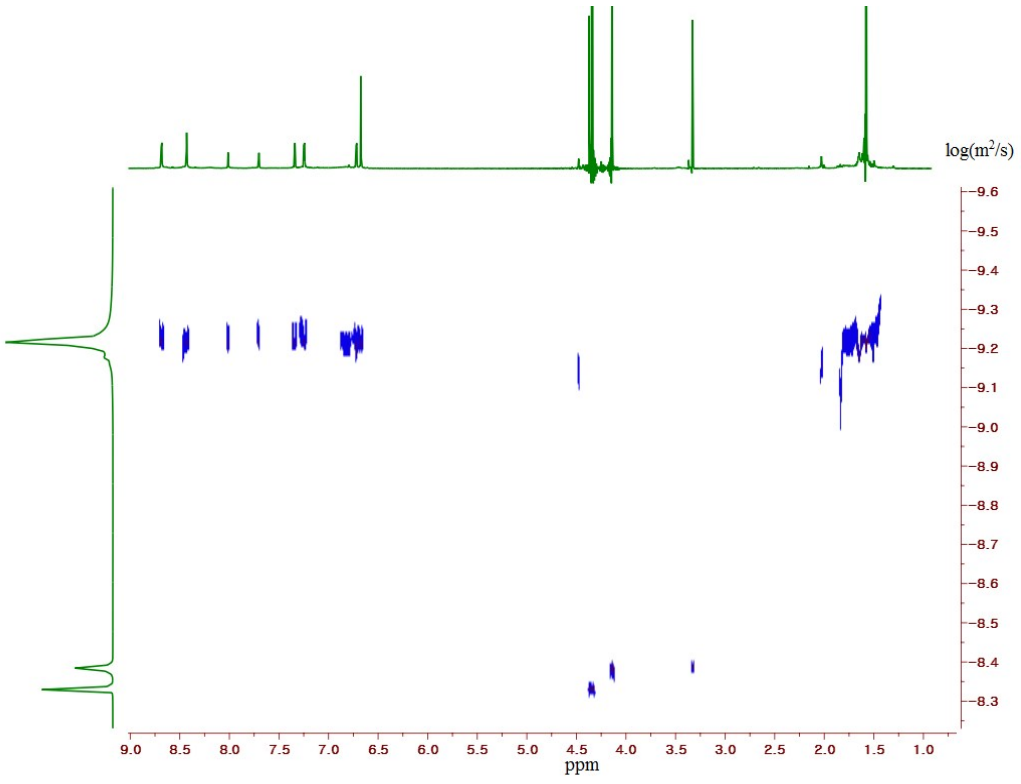


Figure 12S. DOSY NMR spectrum of **[2⊃(G_1•G_2•G_1)]** (1:1 CD_3NO_2/CD_3OD, 298 K, 800 MHz) showing peaks associated with the prismatic cage encapsulated guests with diffusion coefficient of $6.22X10^{-10}$ m^2/sec.

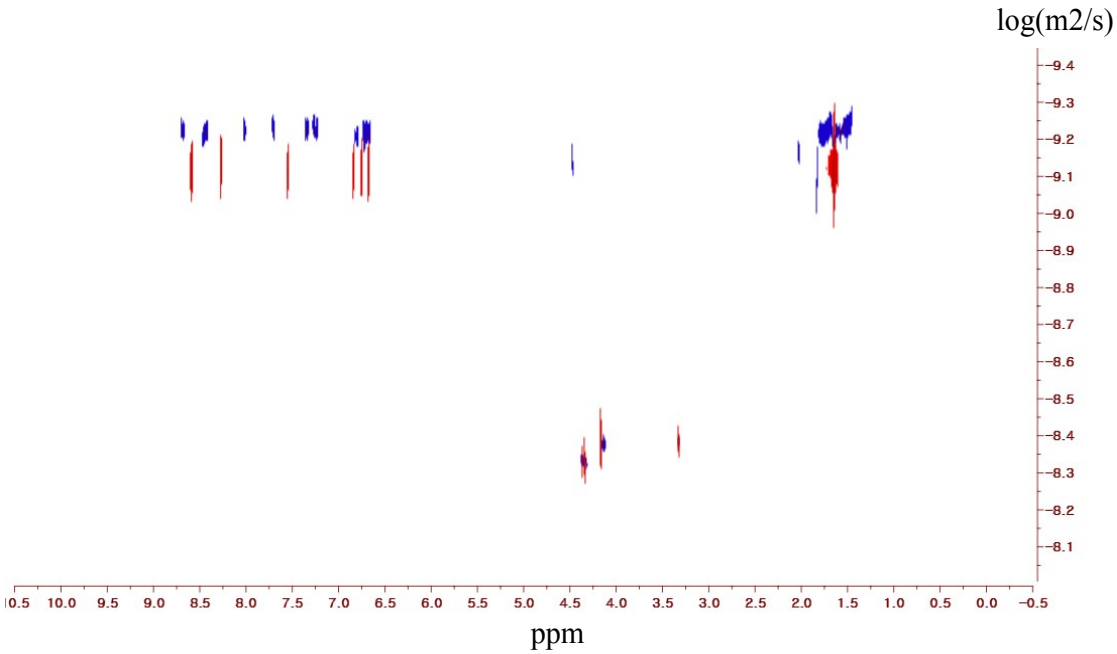


Figure 13S. Comparison of DOSY NMR spectrum of **2**(red) and **[2⊃(G_1•G_2•G_1)]**(blue)

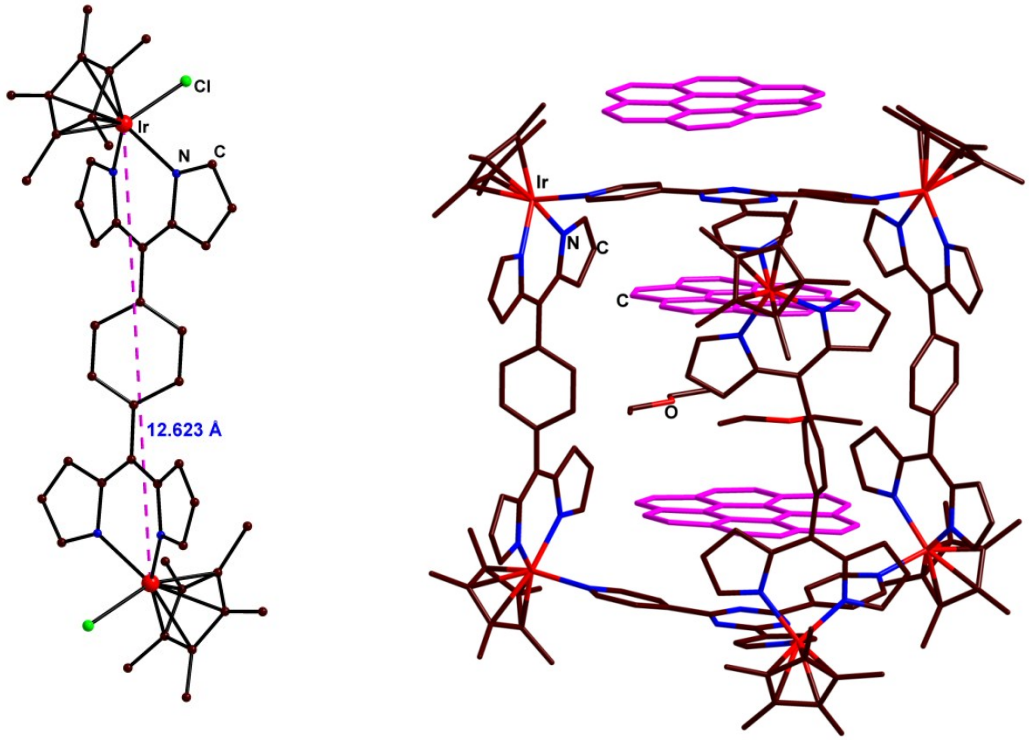


Figure 14S. Crystal structure of **1** showing metal-metal distance in the acceptor clip and crystal structure of **[2⊃(G_1)$_2$]** showing two ether molecules trapped inside the cage and a free coronene molecule stacked outside the cage

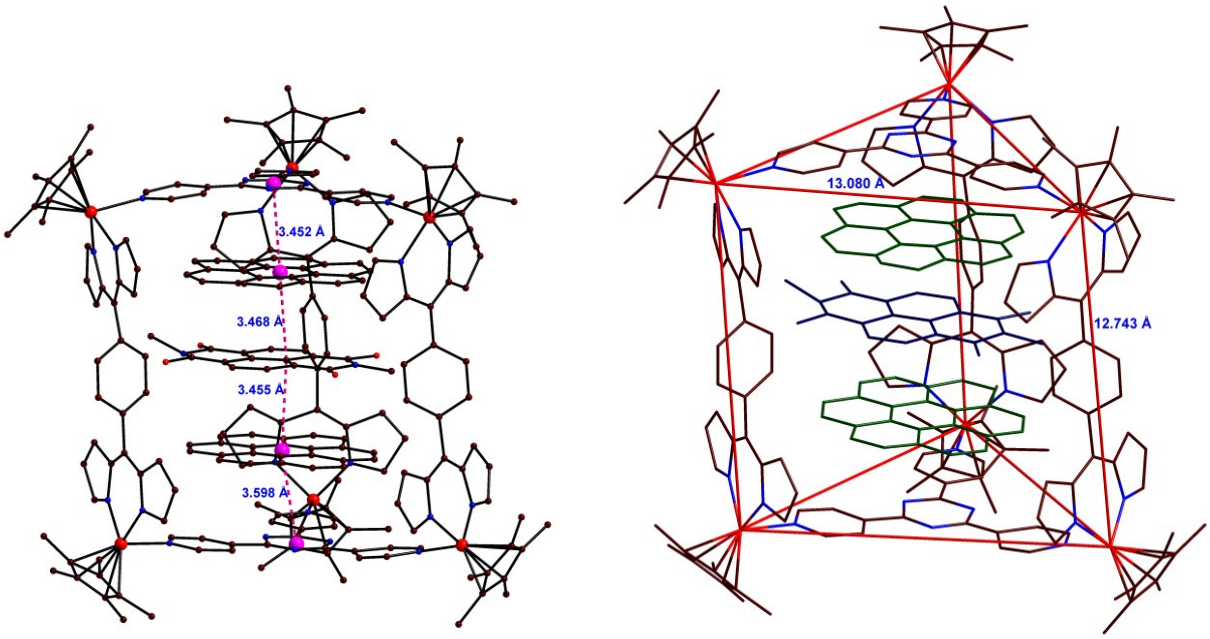


Figure 15S. Crystal structure of **[2⊃(G_1•G_2•G_1)]** showing distances between stacked aromatics (left) and another view showing nearly perfect trigonal prismatic structure of **[2⊃(G_1•G_2•G_1)].**

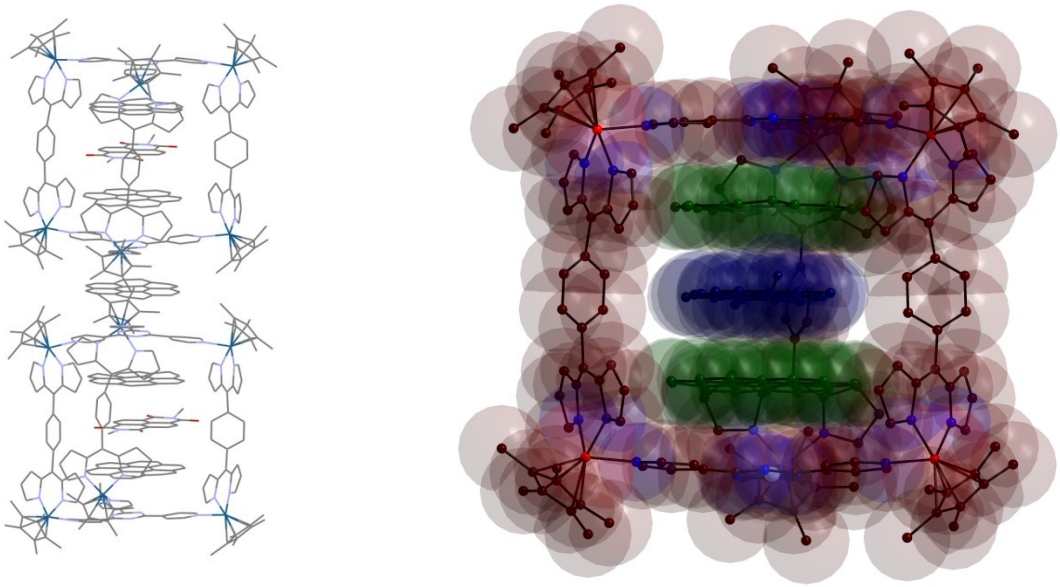


Figure 16S. Crystal structure of **G_1•G_2•G_1)]** showing a coronene molecule stacked between the two molecules and another view showing superimposed space filling model

Reference

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