Supporting Information

Fluorescence enhancement via structural rigidification inside a self-assembled Pd_4 molecular vessel

Shakil Ahmed,[a†] Prodip Howlader,[a†] Soumalya Bhattacharyya,[a] Surajit Mondal,[a] Ennio Zangrando [b] and Partha Sarathi Mukherjee [a]*

[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560012, India

[b] Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste 34127, Italy

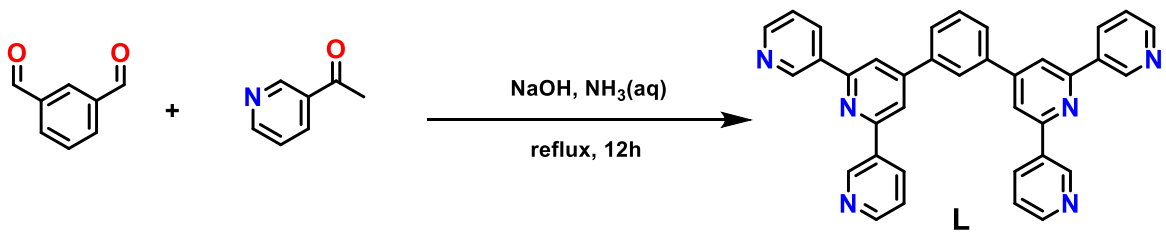
Experimental section:

Methods and materials:

Reagents used in this study were purchased from commercial sources and used without any purification. NMR studies were performed using a Bruker-make 400 MHz spectrometer and the chemical shifts (δ) in the spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvents $CDCl_3$ (7.26 ppm) and D_2O (4.79 ppm). The guest **SG** was synthesized according to the reported procedure.[1]

Synthesis of the ligand L:

The ligand **L** was synthesized following reported procedure of terpyridine synthesis. Isopthaldehyde (670 mg, 5 mmol) was taken into a flame dried 500 mL round bottom flask containing 50 mL of ethanol at 0 °C followed by addition of NaOH (400 mg, 10 mmol) with stirring. To this cold solution 3-acetyl pyridine (2.42 g, 20 mmol) in 10 mL of ethanol was added dropwise. Finally, 60 mL of ammonia solution was added followed by stirring at 0 °C for 1 h. The solution was then allowed to reach room temperature and refluxed at 80 °C for 12 h. The precipitate formed after refluxing was filtered and washed thoroughly with ethanol and water to get solid powder of **L** as pure product. Yield 1.50 g (56 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (s, 4H), 8.71-8.70 (d, 4H), 8.54-8.52 (d, 4H), 8.06-8.01 (s, 5H), 7.89-7.87 (d, 2H), 7.78-7.76 (d, 1H), 7.49-7.46 (d, 4H).



Scheme S1: Synthetic scheme for ligand **L**.

Synthesis of the cage MP1:

cis-(en)Pd(NO_3)$_2$ (**M1**) (6.9 mg, 0.024 mmol) was dissolved in 0.5 mL of H_2O-CH_3OH (7:3) mixture and the yellow clear solution was added to the solid ligand **L** (6.45 mg, 0.012 mmol) and heated at 60 °C with stirring for 12 h resulting in clear colourless solution. The clear solution was then subjected to acetone vapour diffusion and within a week formation of colourless hexagonal shaped crystals was observed. These single crystals were further used for SC-XRD analysis to determine the structure. Similar reaction was carried out in deuterated solvent for recording the ^{1}H NMR spectra. ^{1}H NMR (400 MHz, D_2O-CD_3OD): δ = 10.25 (s, 8H), 9.08-9.07 (d, 8H), 8.59-8.58 (d, 8H), 8.08 (s, 8H), 7.84-7.82 (d, 4H), 7.70-7.68 (t, 8H), 7.60-7.59 (d, 4H), 3.27-3.26 (m, 16H).

Synthesis of the cage MP2:

cis-(dmen)Pd(NO_3)$_2$ (**M2**) (7.6 mg, 0.024 mmol) was dissolved in 0.5 mL of H_2O-CH_3OH (1:1) mixture and the yellow clear solution was added to the solid ligand **L** (6.45 mg, 0.012 mmol) and heated at 60 °C with stirring for 12 h resulting in clear colourless solution. The clear solution was then treated with excess of KPF_6 to get white coloured precipitate. The white precipitate was then isolated and dissolved in acetonitrile followed by ESI-MS spectroscopy study. Similar reaction was carried out in deuterated solvent for recording 1D and 2D ^{1}H NMR spectra.

Host-guest encapsulation with MP1:

Molecular pocket **MP1** was synthesized according to the above-mentioned procedure in deuterated solvent. Then different guests in excess amount were added to the clear solution of **MP1** in D_2O:CD_3OD mixture and the mixture was stirred for 12 h. The mixture was then centrifuged, and the excess solid was discarded to get a clear solution of the host-guest complex. All these solutions were characterized by ^{1}H NMR and ^{1}H DOSY and ^{1}H NOESY spectroscopy.

Single crystal structure of MP1:

Single crystal X-ray data for **MP1** were collected on X-ray diffraction beamline XRD1 of the ELETTRA Synchrotron, Trieste (Italy), using the rotating crystal method with a monochromatic wavelength of 0.7000 Å, on a Dectris Pilatus 2M detector. Data collection was done at 100(2) K using a nitrogen stream cryo-cooler. Cell refinement, indexing and scaling of the data set were performed using the CCP4 package, and programs Denzo and Scalepack. The structure was solved by intrinsic phasing method with ShelXT[1] and refined by the full-matrix least-squares method based on F^2 with all observed reflections using the Olex2 program.[2] All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon were included at geometric positions and given thermal parameters equivalent to 1.2xtimes those of the atom to which they were attached. In addition, the structure contains a huge void of disordered solvent molecules therefore, solvent mask incorporated in the program was applied to account for embedded solvent molecules.[3] Crystallographic data and refinement parameter are given in **Table S1**.

Table S1: Crystallographic data and refinement parameters of **MP1**

empirical formula	$C_{86}H_{92}N_{28}O_{27}Pd_4$
Fw	2375.47
T /K	100(2)
crystal system	triclinic
space group	*P*-1
a /Å	16.423(3)
b /Å	18.511(4)
c /Å	22.079(4)
α /deg	83.12(3)
β /deg	71.77(3)
γ /deg	65.34(3)
V /Å³	5793(3)
Z	2
ρ_{calcd} ***/g cm⁻³***	1.362
μ (Mo-Kα) /mm⁻¹	0.663
λ /Å	0.700
F(000)	2408.0
collected reflns	229558
unique reflns	37584
GOF on F²	1.038
R₁ [a]	0.0573
wR₂ [b]	0.1528
CCDC No.	2179640

[a] $R_1=\Sigma\big|\,|F_o|-|F_c|\,\big|/\Sigma|F_o|$, [b] $wR_2=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

Computational studies:

Full geometry optimization of **SG⊂MP1** (Figure S25) was carried out by semi-empirical method with PM6 basis set using the Gaussian 09 package. Finally, single-point energy of the host-guest complex was calculated using the hybrid B3LYP functional with a mixed basis set of LanL2DZ (for Pd atom) and 631g (for C, H, and N atoms).

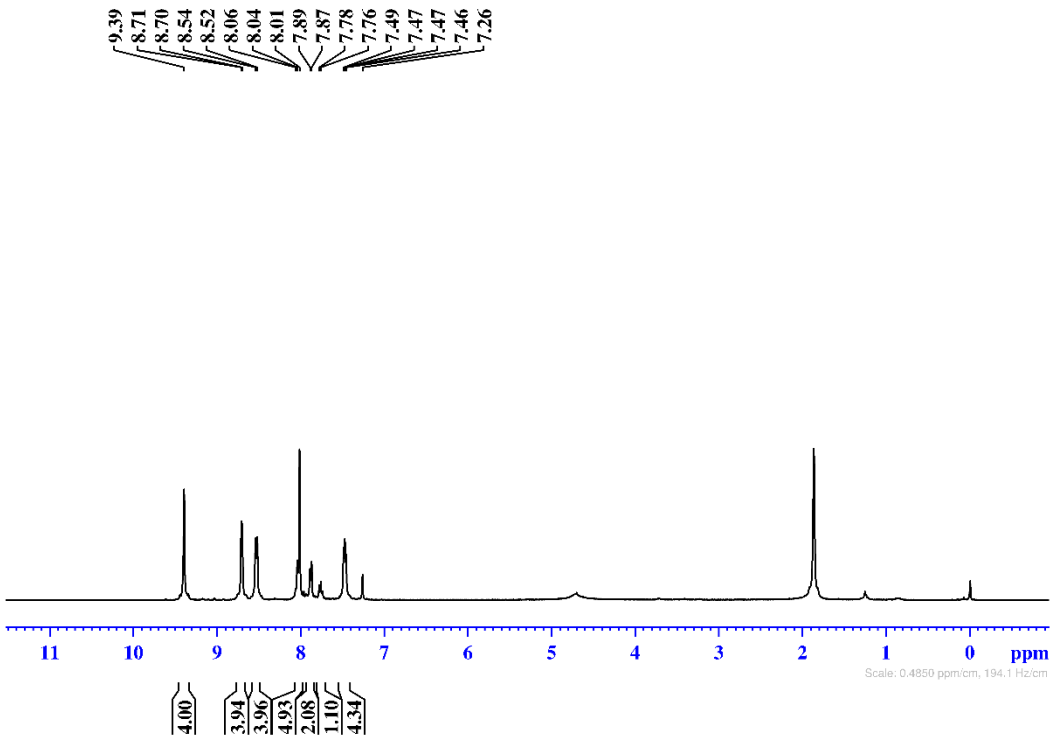


Fig. S1: ^{1}H NMR spectrum of the ligand **L** in $CDCl_3$.

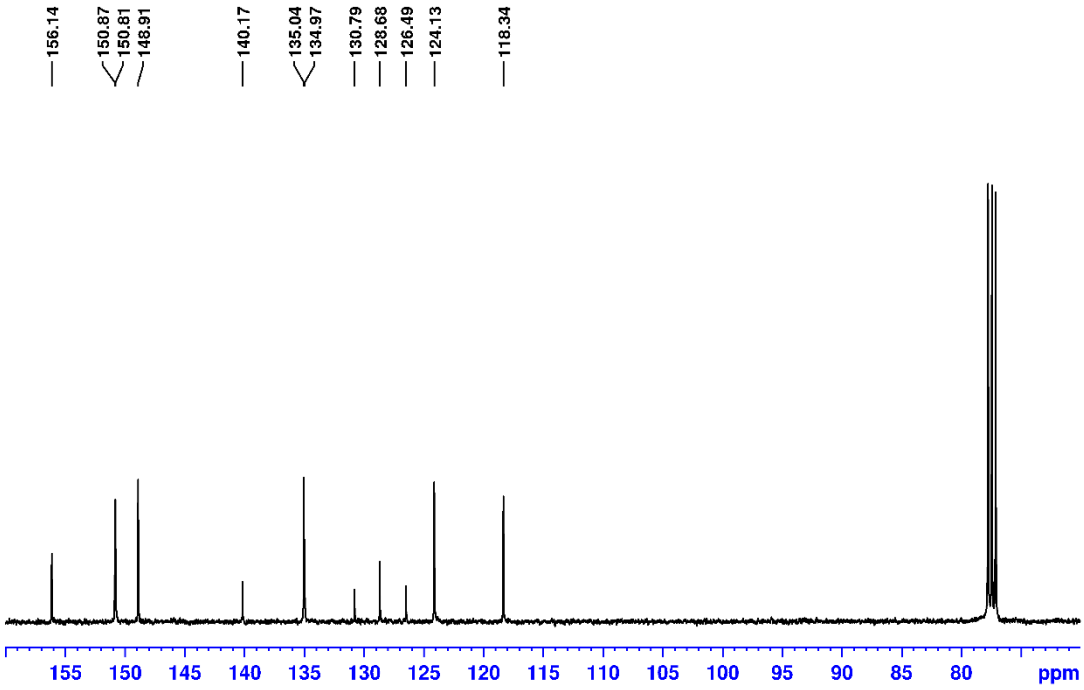


Fig. S2:^{13}C NMR spectrum of the ligand **L** in $CDCl_3$.

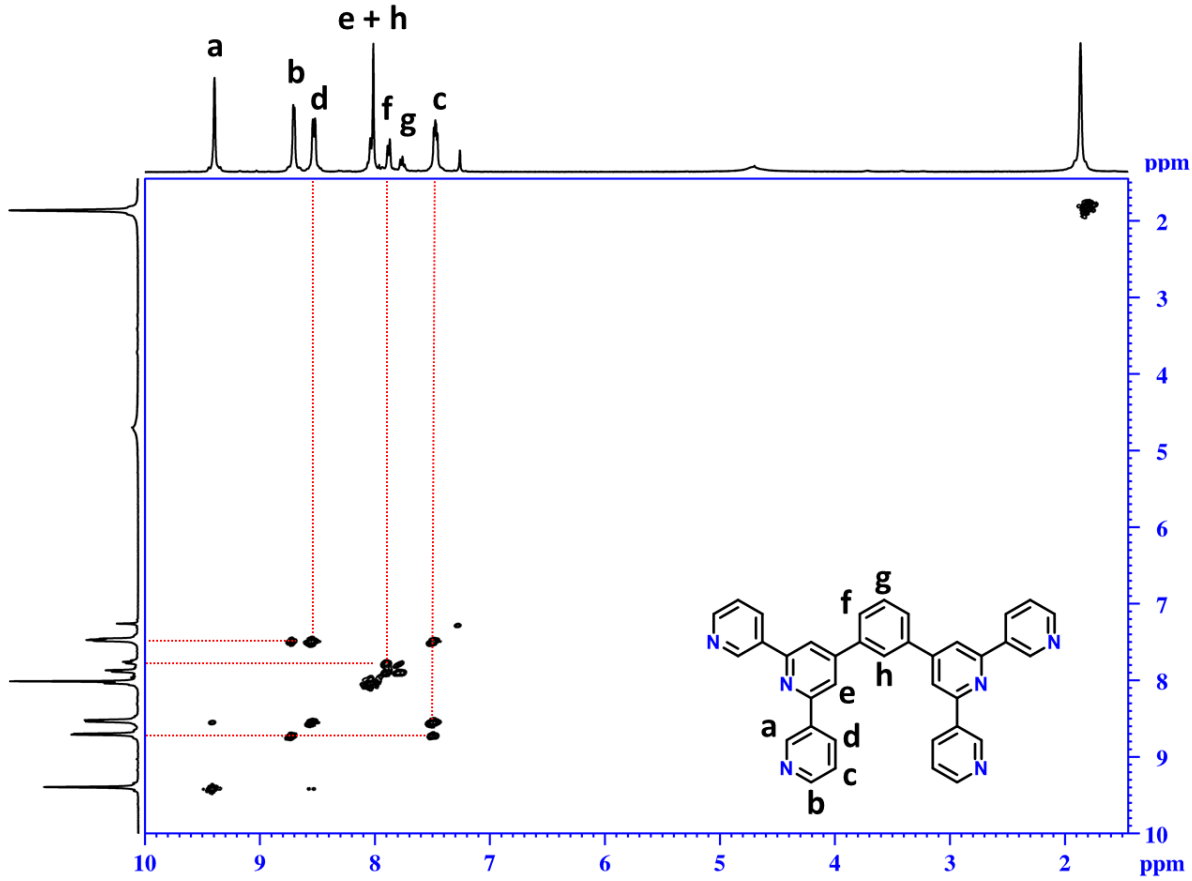


Fig. S3: ^{1}H-^{1}H COSY NMR of the ligand **L** in $CDCl_3$.

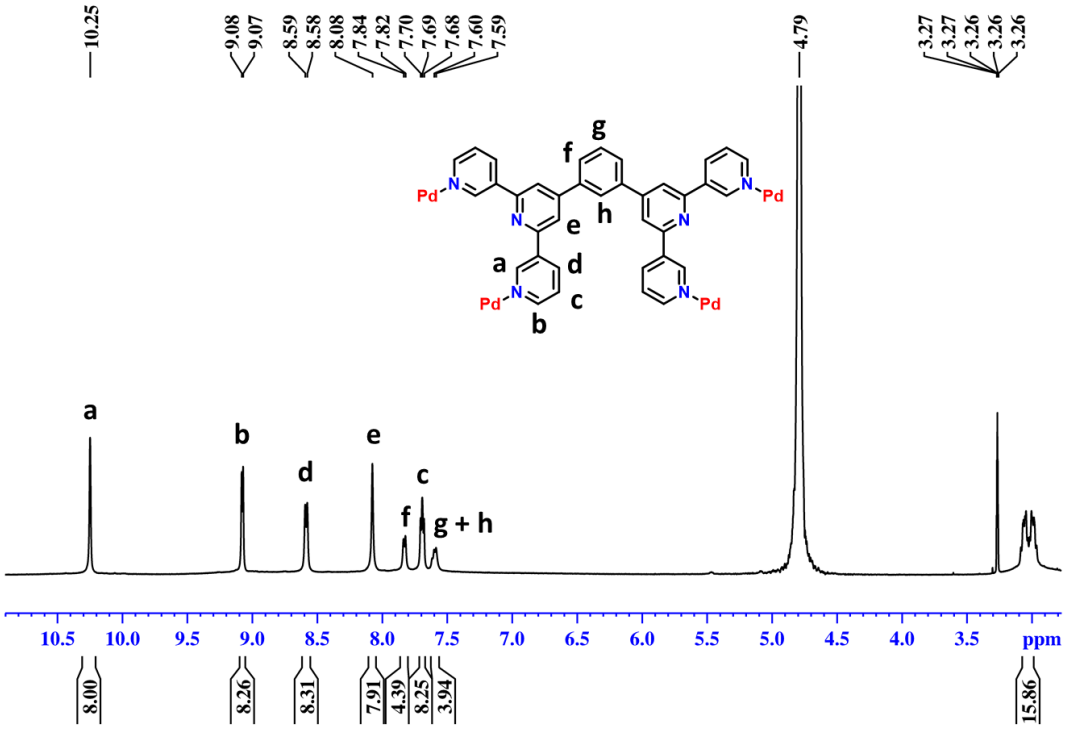


Fig. S4: ^{1}H NMR spectrum of **MP1** in D_2O-CD_3OD (7:3) mixture.

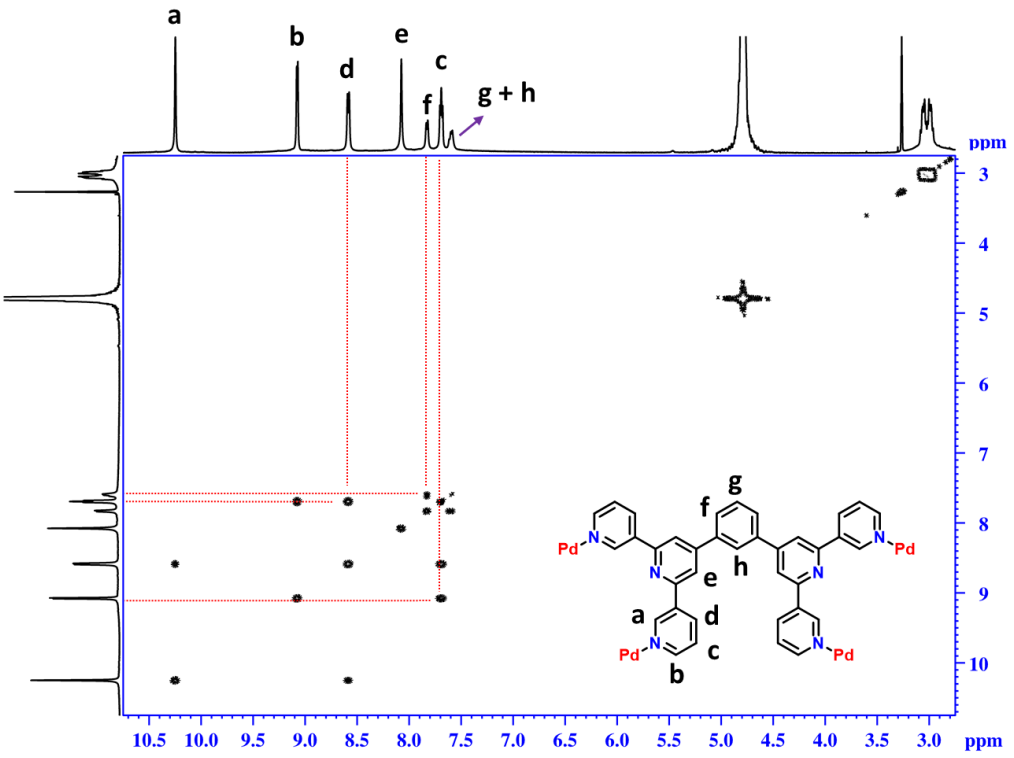


Fig. S5: ^{1}H-^{1}H COSY NMR of **MP1** in D_2O-CD_3OD (7:3) mixture.

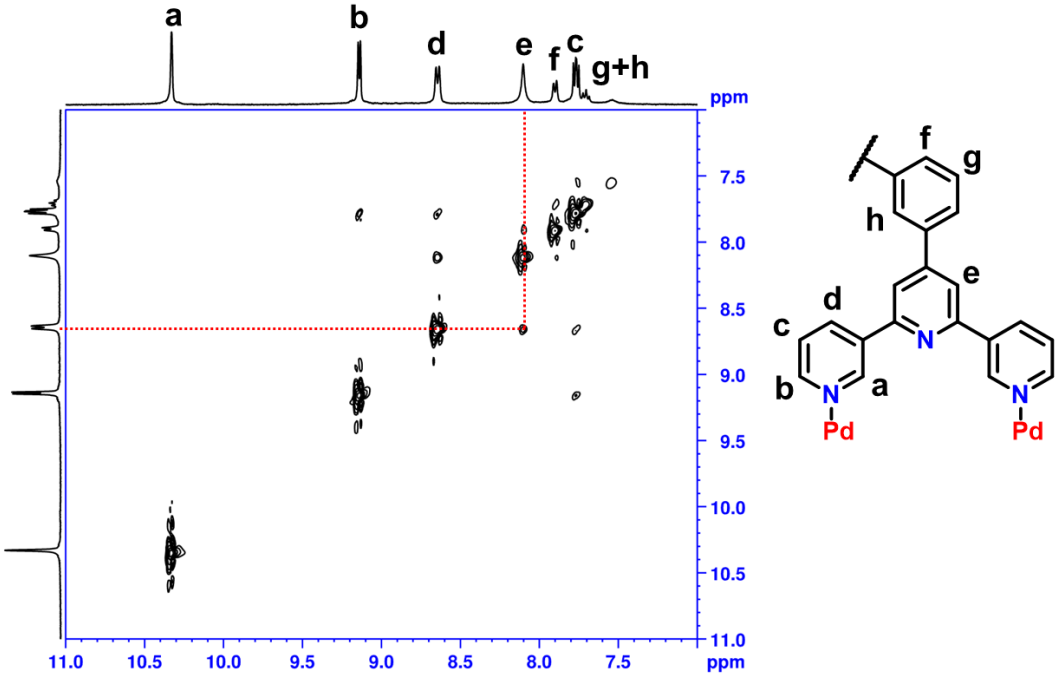


Fig. S6: ^{1}H-^{1}H NOESY NMR of the **MP1** in D_2O-CD_3OD (7:3) mixture.

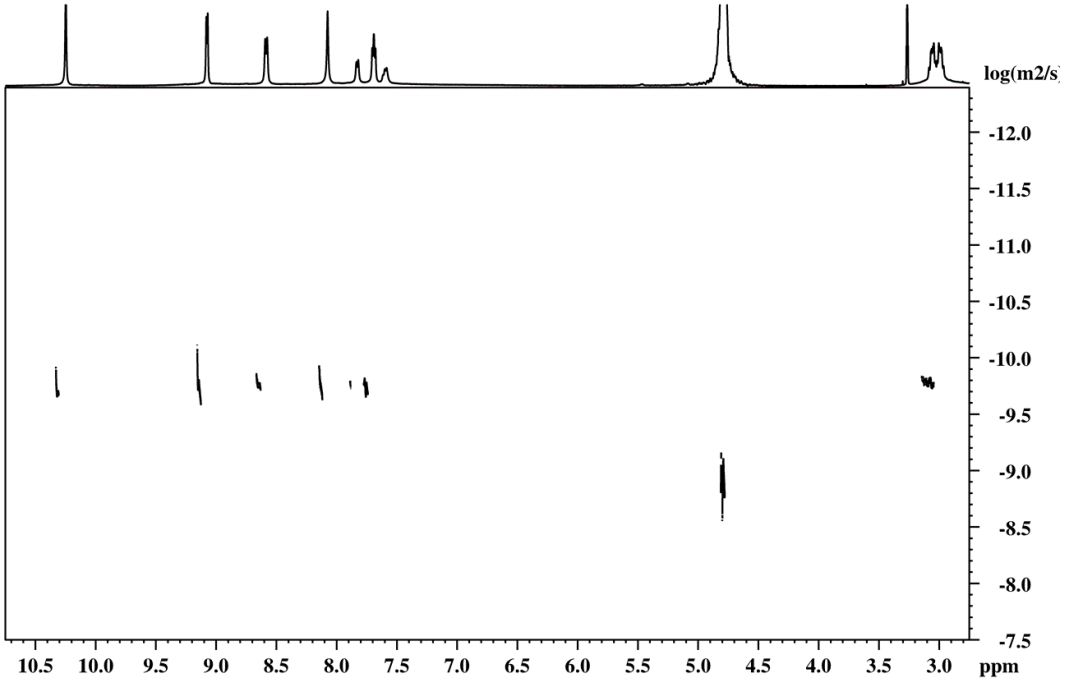


Fig. S7: ^{1}H DOSY NMR spectrum of the **MP1** in D_2O-CD_3OD (7:3) mixture.

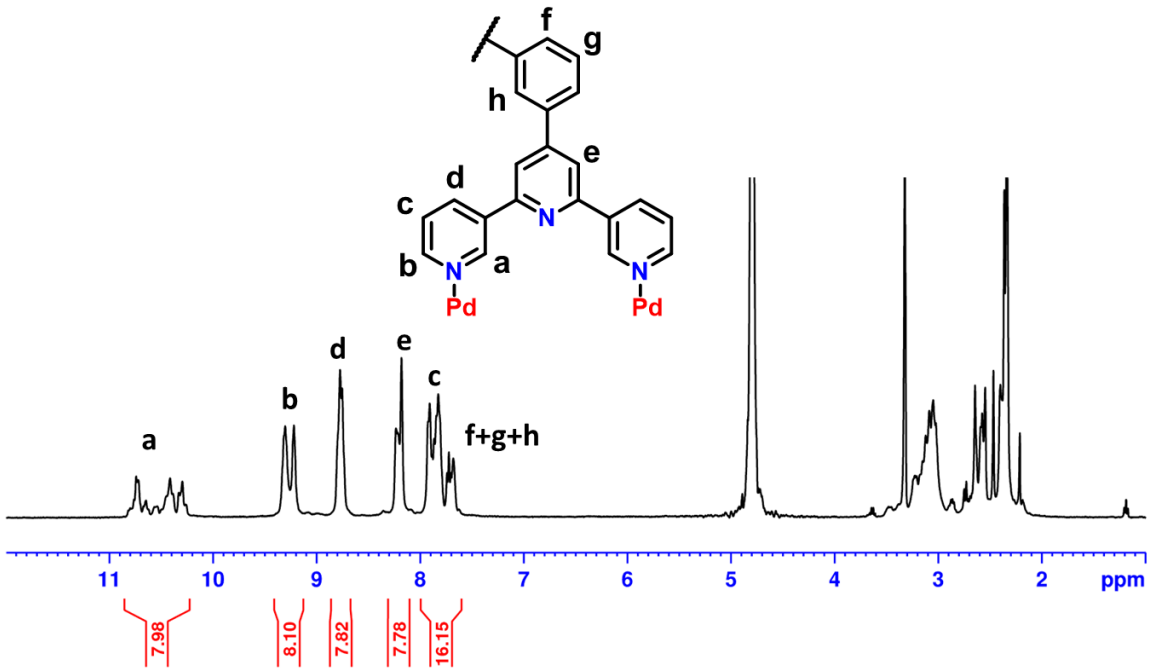


Fig. S8: ^{1}H NMR spectrum of **MP2** in D_2O-CD_3OD (1:1) mixture.

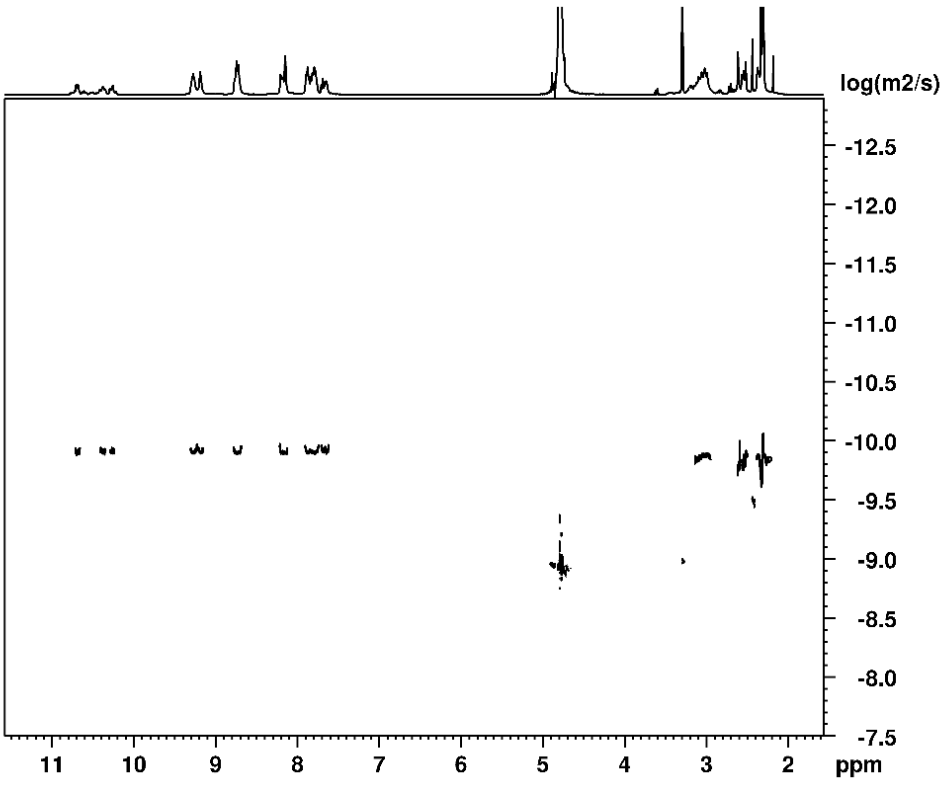


Fig. S9: ^{1}H DOSY NMR of **MP2** in D_2O-CD_3OD (1:1) mixture.

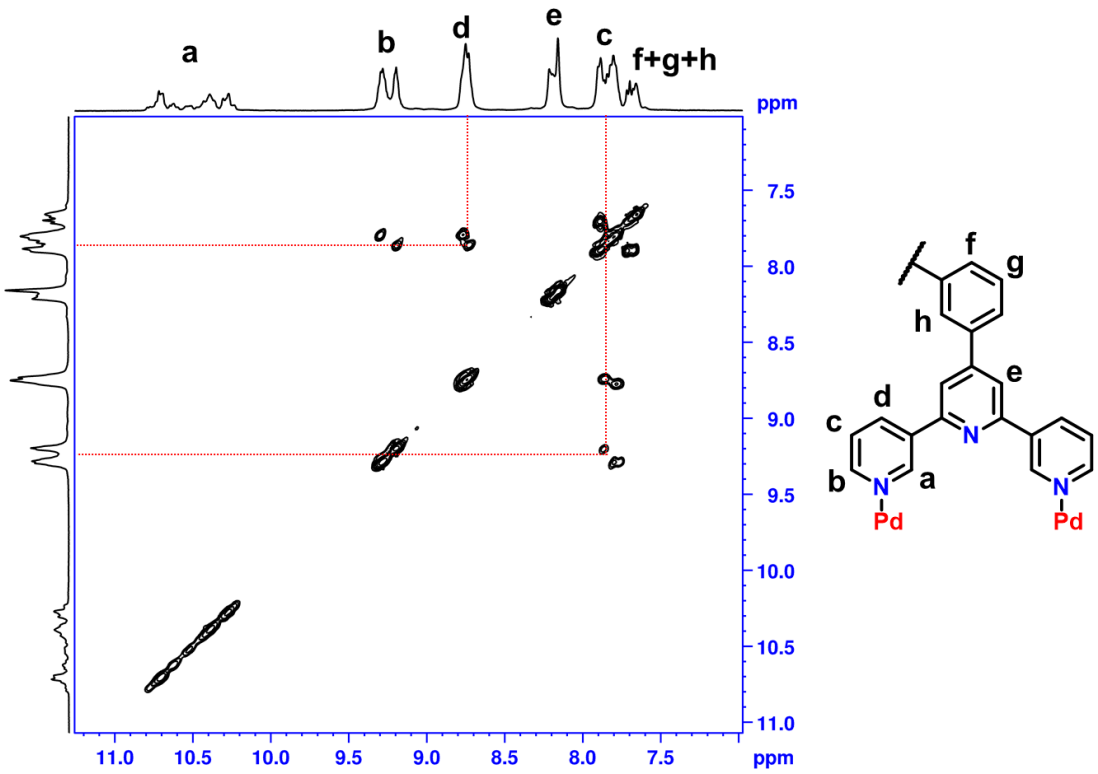


Fig. S10: ^{1}H-^{1}H COSY NMR spectra of the **MP2** in D_2O-CD_3OD (1:1) mixture.

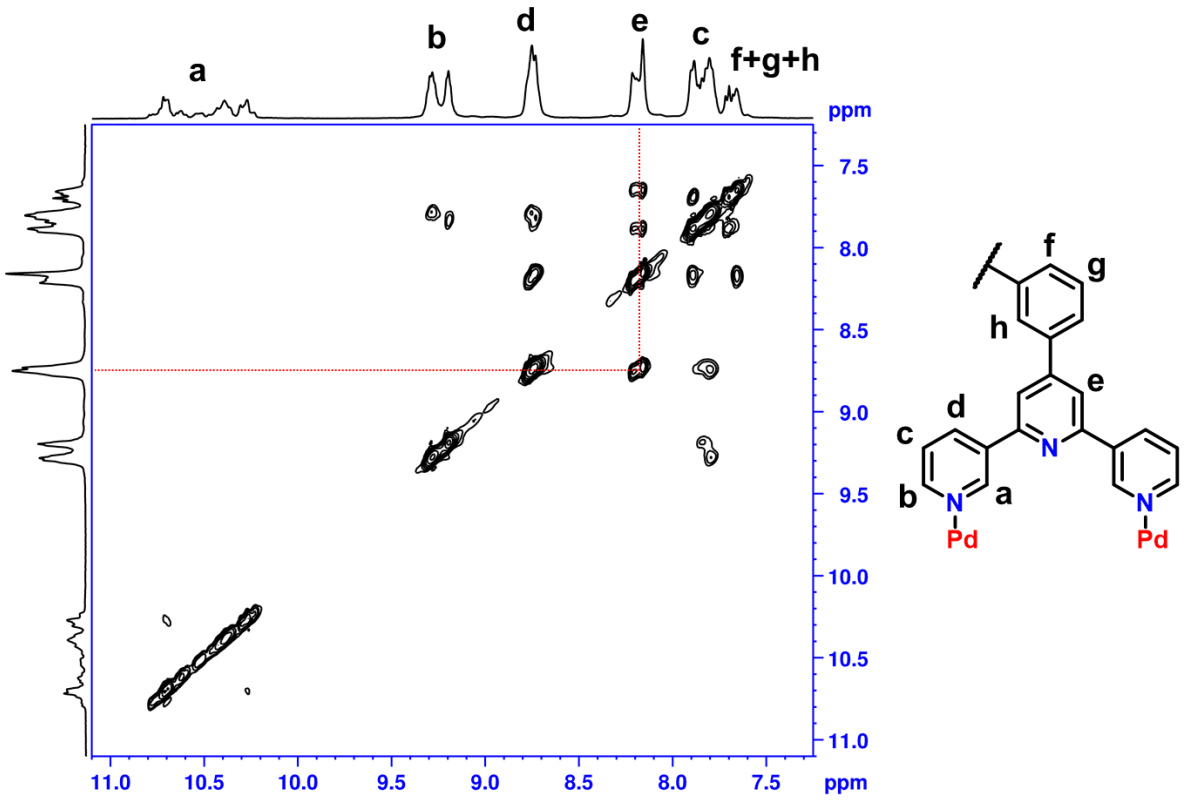


Fig. S11: ^{1}H-^{1}H NOESY NMR spectrum of **MP2** in D_2O-CD_3OD (1:1) mixture.

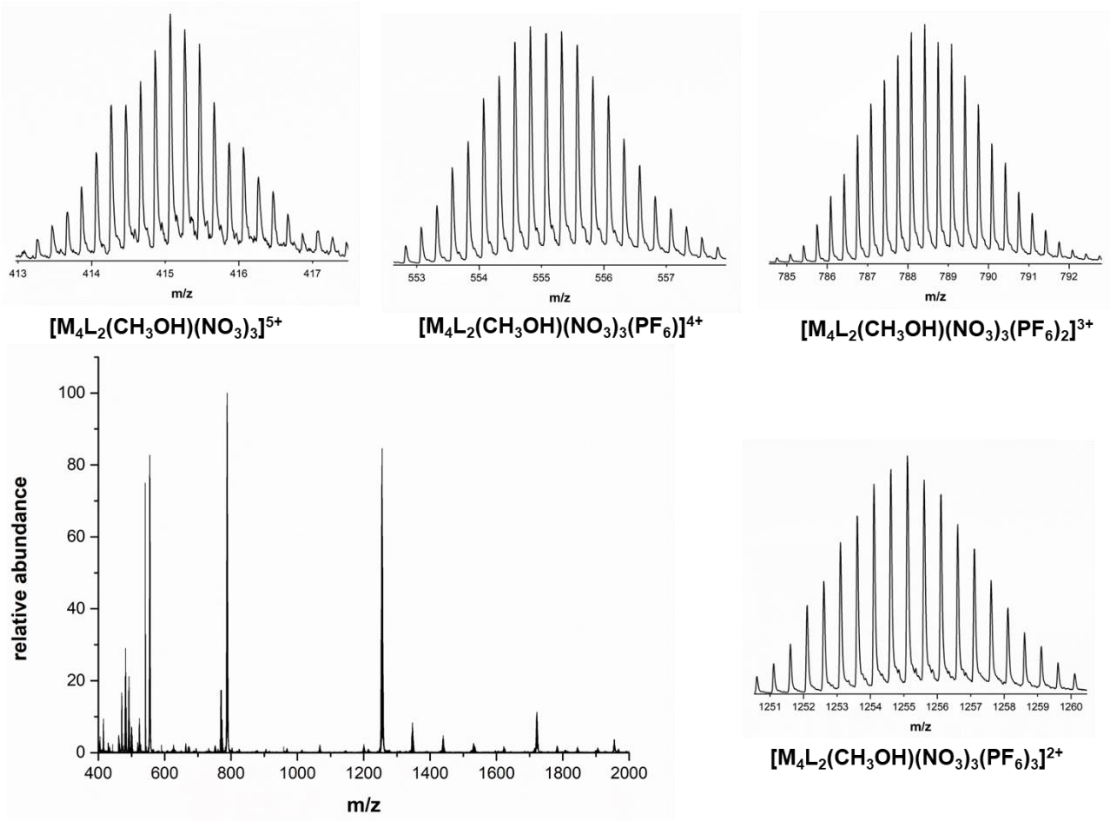


Fig. S12: ESI-MS spectrum of PF_6^- analogue salt of **MP2** in acetonitrile containing 5% of methanol.

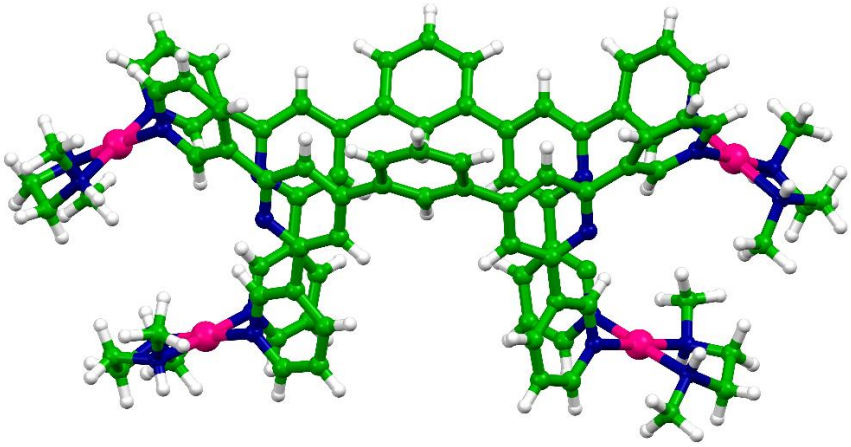


Fig. S13: Energy optimized geometry of **MP2**. Color codes: Pd pink; N blue; C green; H white.

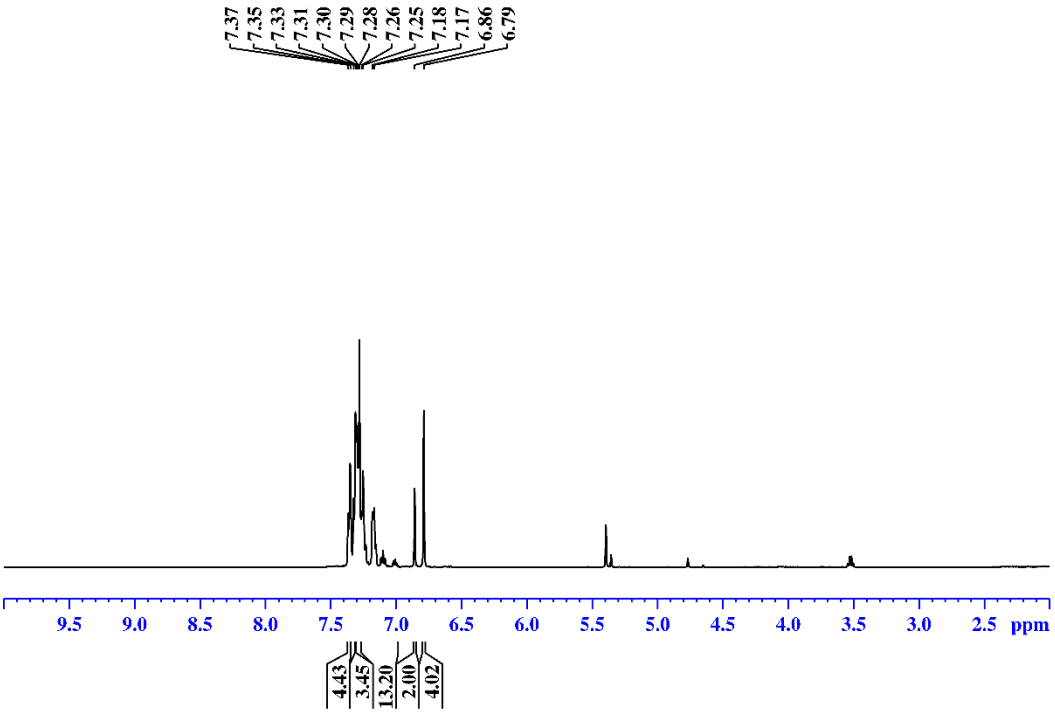


Fig. S14: ^{1}H NMR spectrum of **SG** in $CDCl_3$.

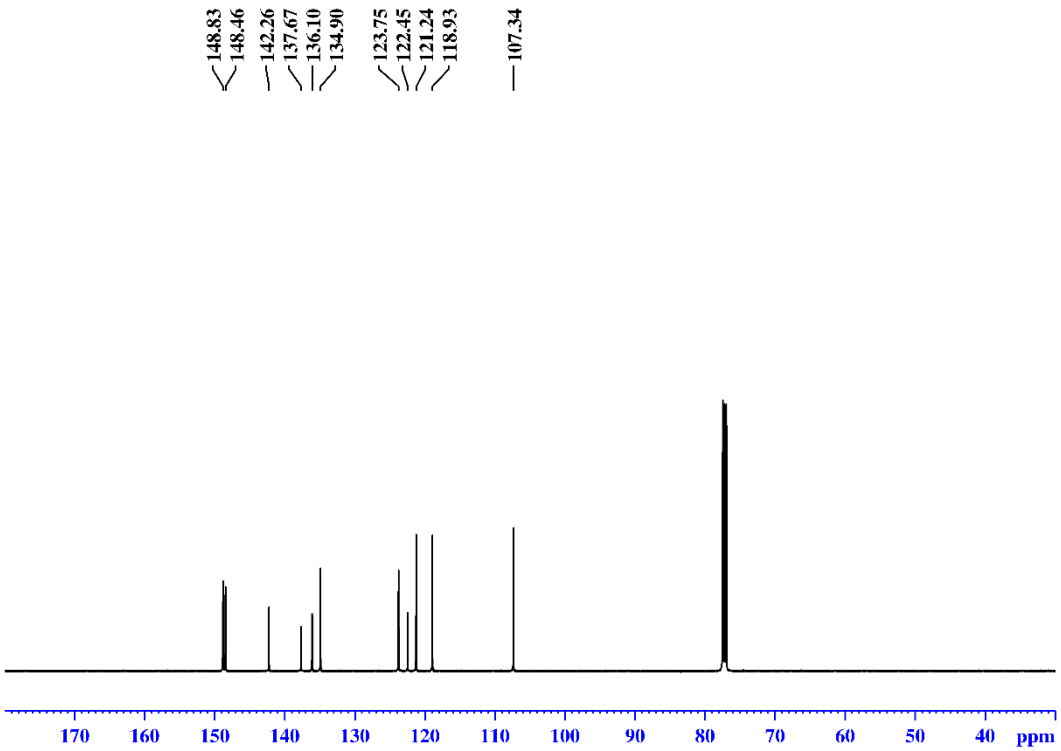


Fig. S15: ^{13}C NMR spectrum **SG** in $CDCl_3$.

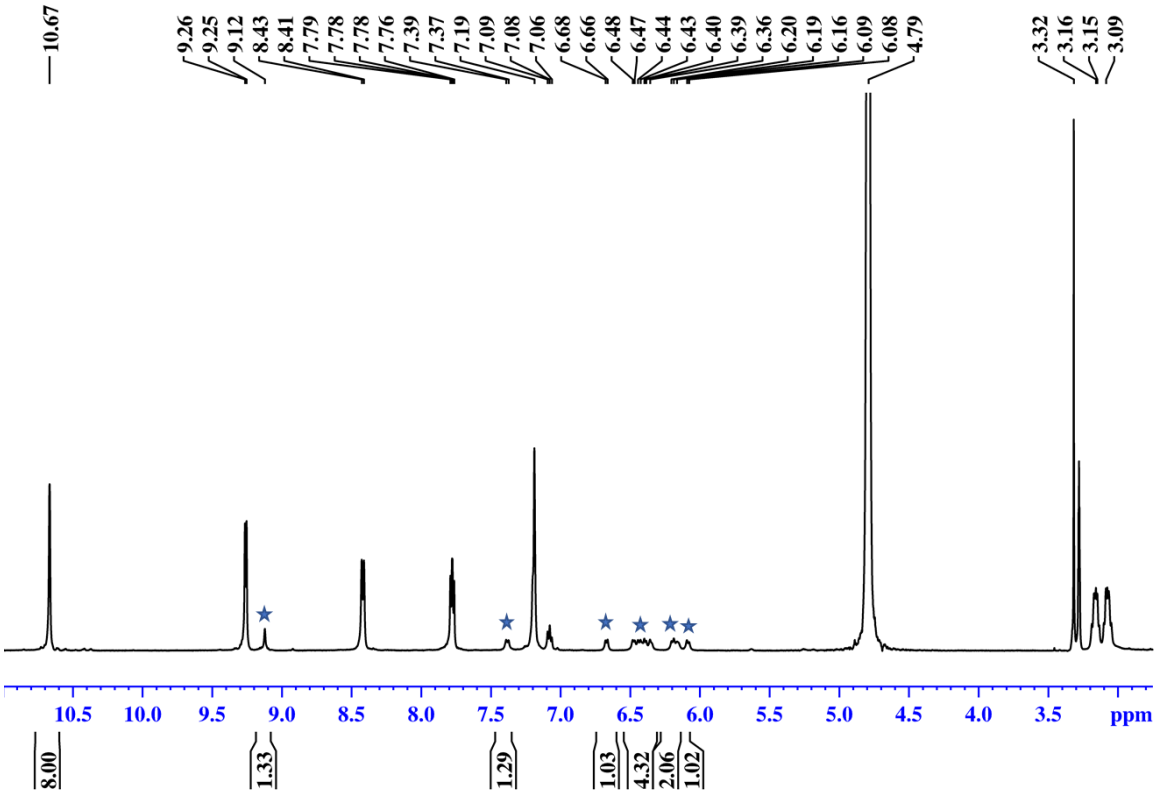


Fig. S16: ^{1}H NMR spectrum of 1-pyrenealdehyde encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture. 1-pyrenealdehyde peaks are denoted by ⋆ shape.

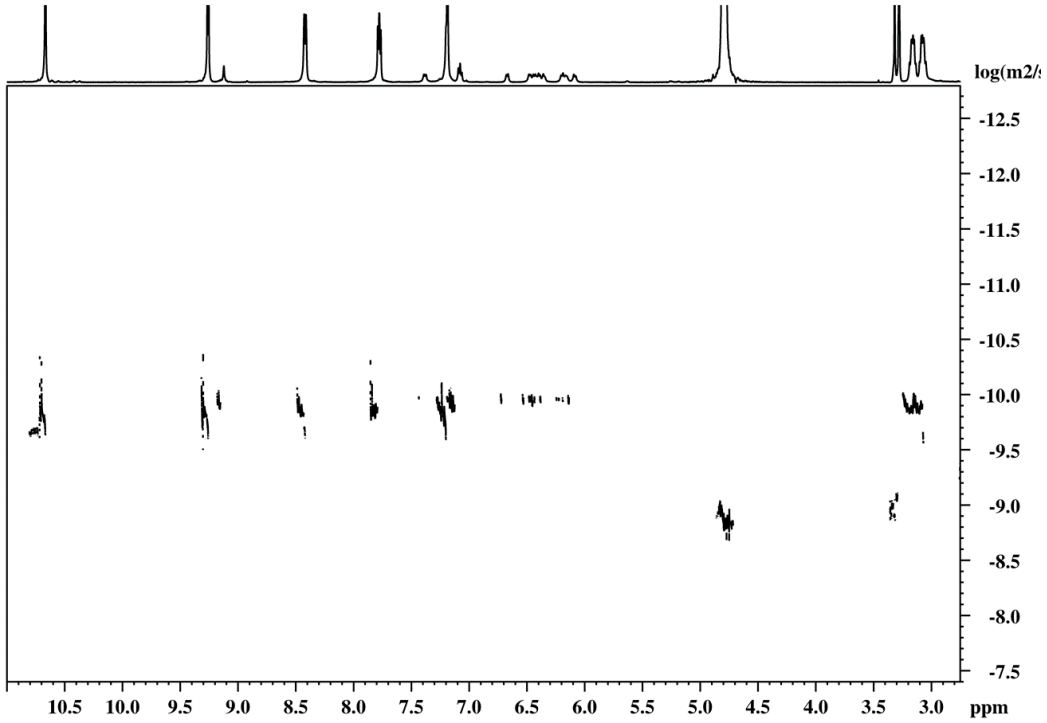


Fig. S17: ^{1}H DOSY NMR spectrum of 1-pyrenealdehyde encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

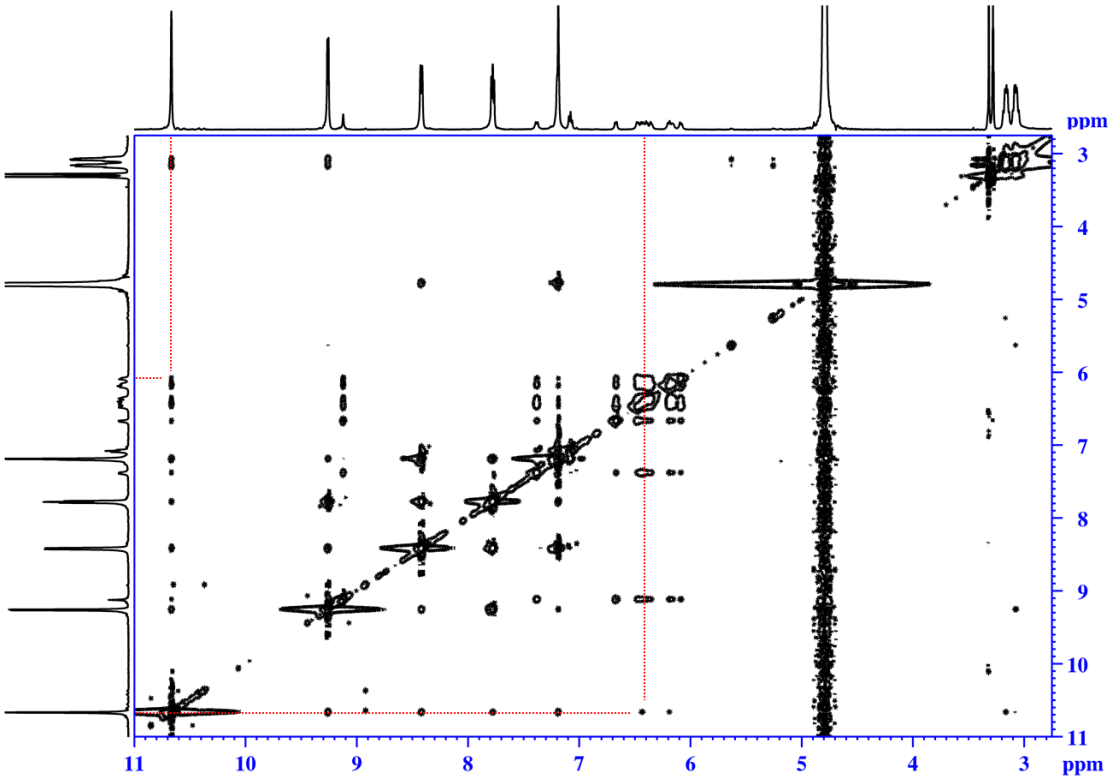


Fig. S18: ^{1}H-^{1}H NOESY NMR of 1-pyrenealdehyde encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

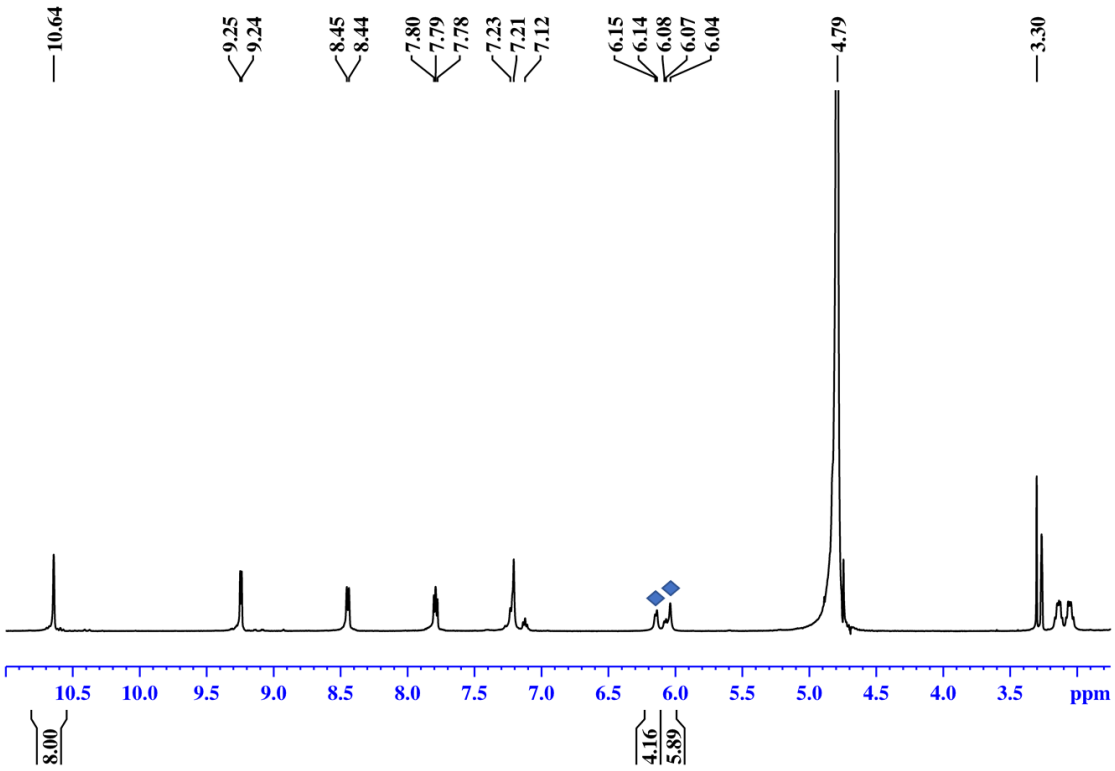


Fig. S19: ^{1}H NMR spectrum of pyrene encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture. Pyrene proton peaks are denoted by ♦ shape.

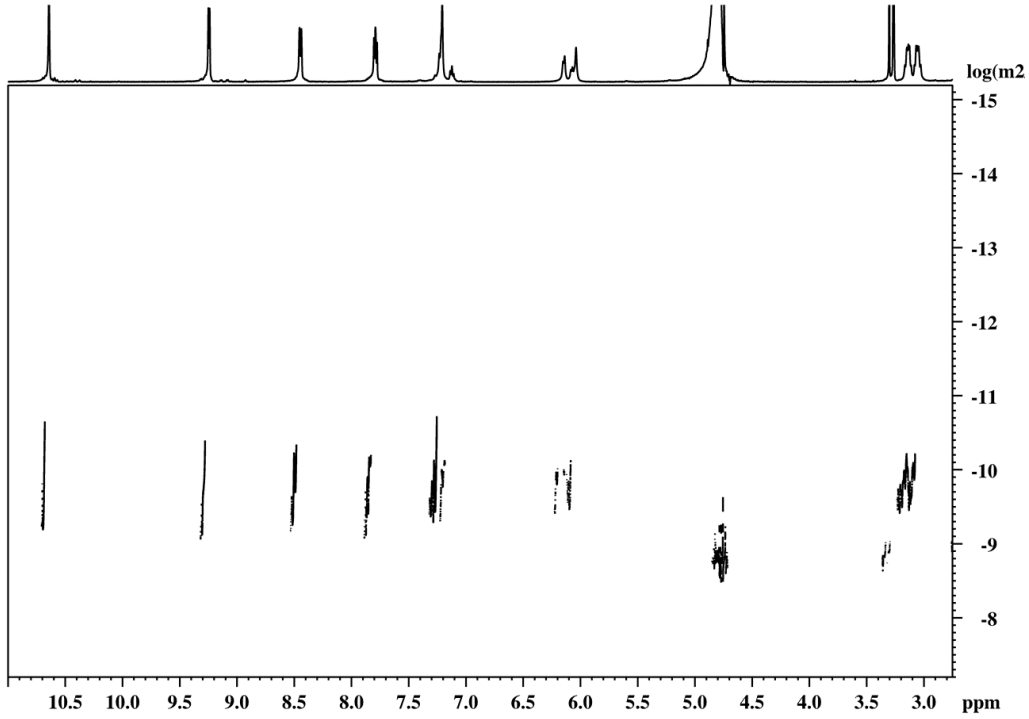


Fig. S20: ^{1}H DOSY NMR of pyrene encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

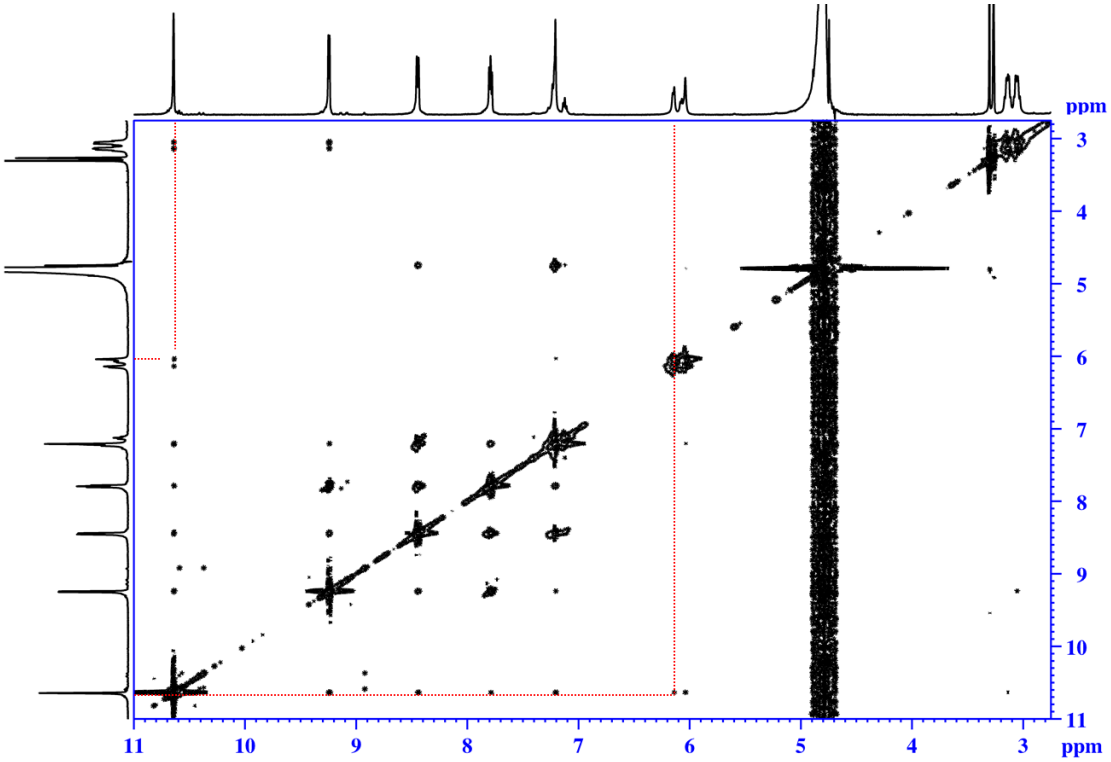


Fig. S21: ^{1}H-^{1}H NOESY NMR of pyrene encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

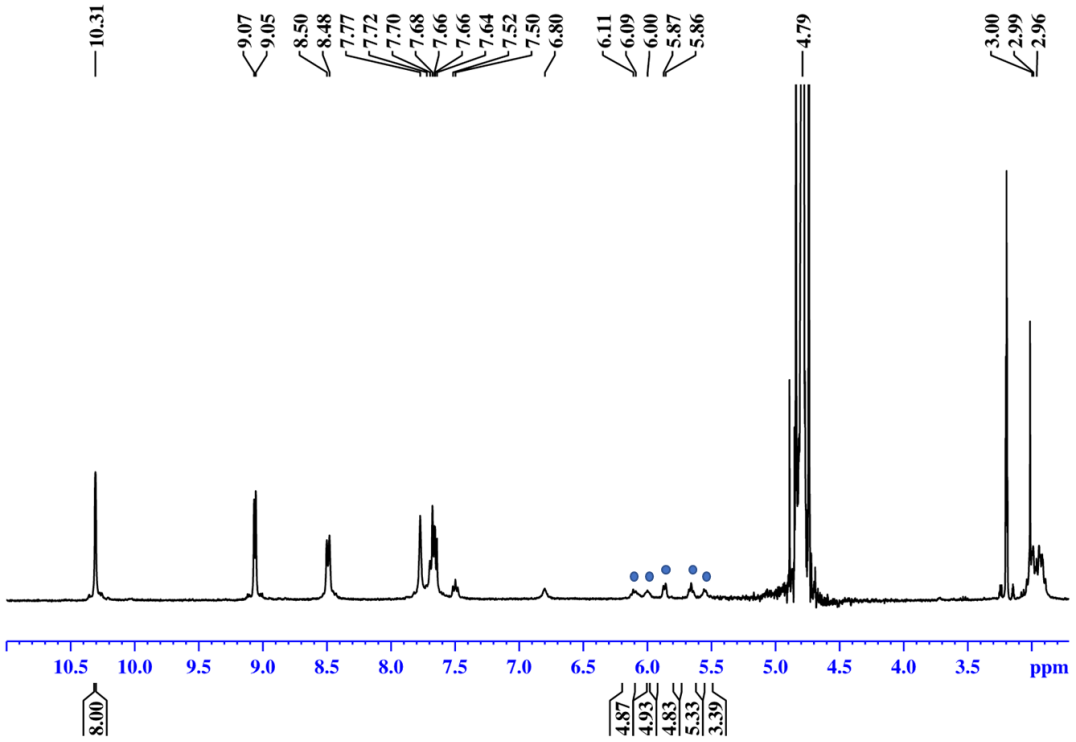


Fig. S22: ^{1}H NMR spectrum of **SG** encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture. Proton peaks of **SG** are denoted by ● shape.

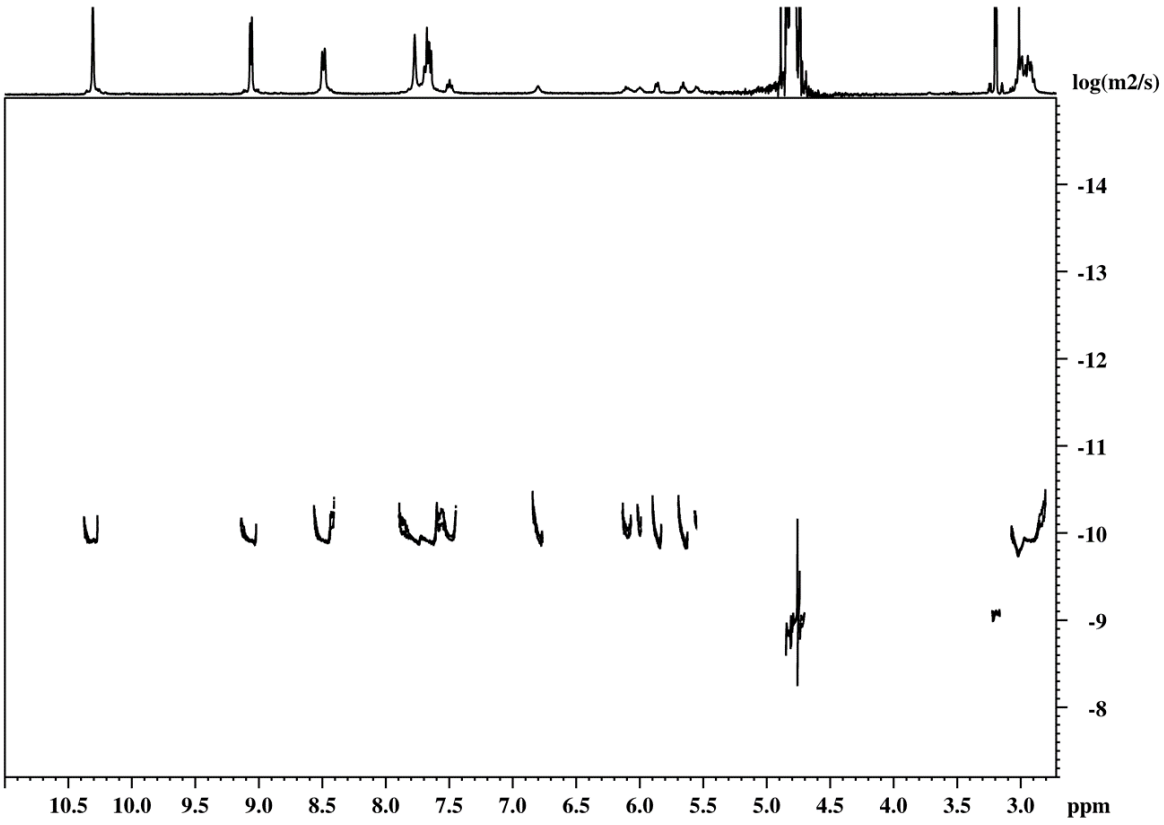


Fig. S23: ^{1}H DOSY NMR spectrum of **SG** encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

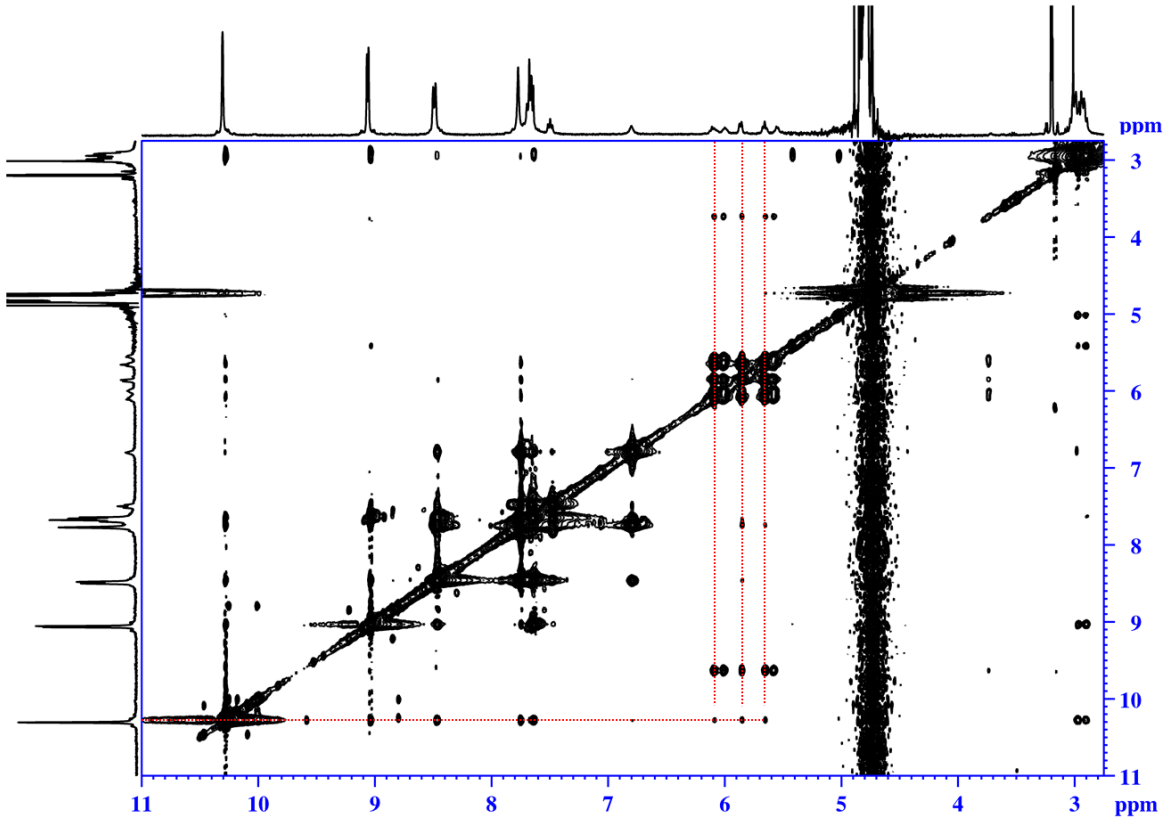


Fig. S24: ^{1}H-^{1}H NOESY NMR spectrum of **SG** encapsulated **MP1** in D_2O-CD_3OD (7:3) mixture.

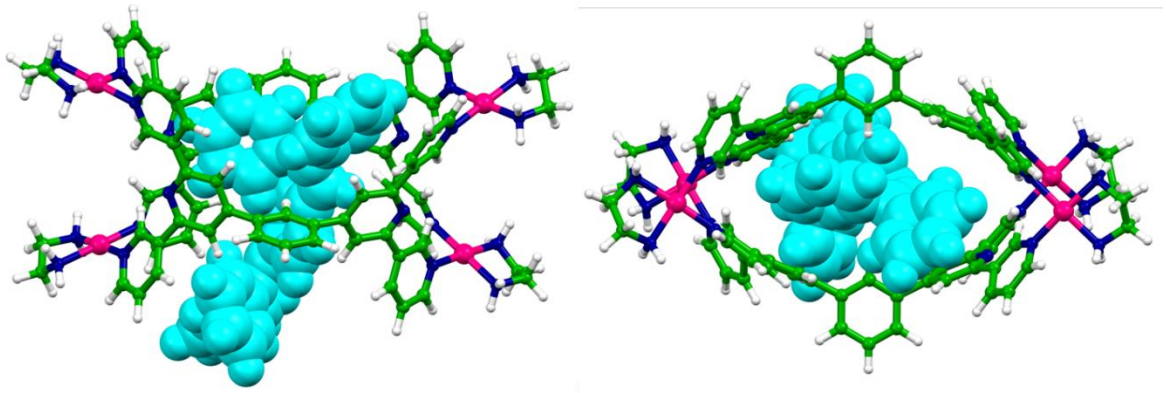


Fig. S25: Energy optimized geometry of **SG⊂MP1**. (a) side view, and (b) top view. Color codes: Pd pink; N blue; C green; H white and the guest molecule as light blue.

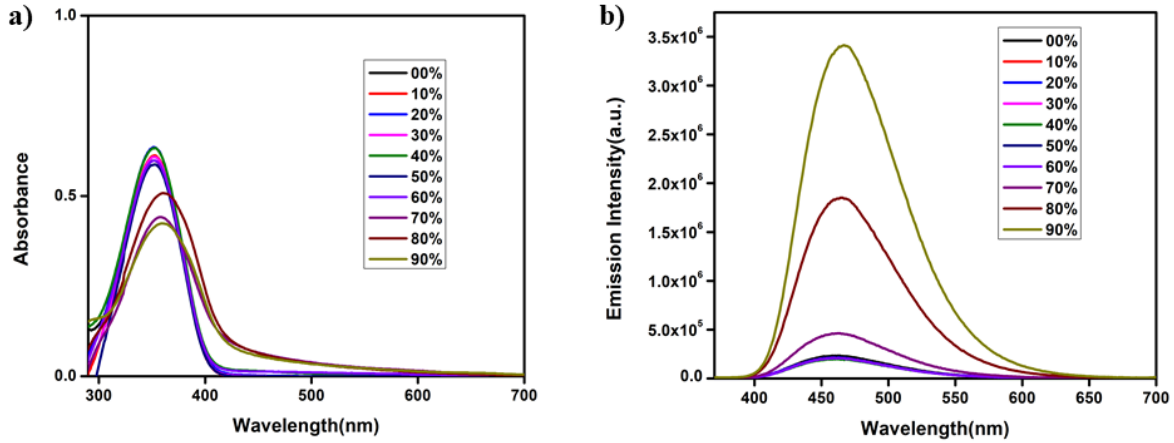


Fig. S26: a) UV-Vis spectra; b) Fluorescence emission spectra of **SG** corresponding to different water fractions in THF ([**SG**] = 1.7×10^{-6} M).

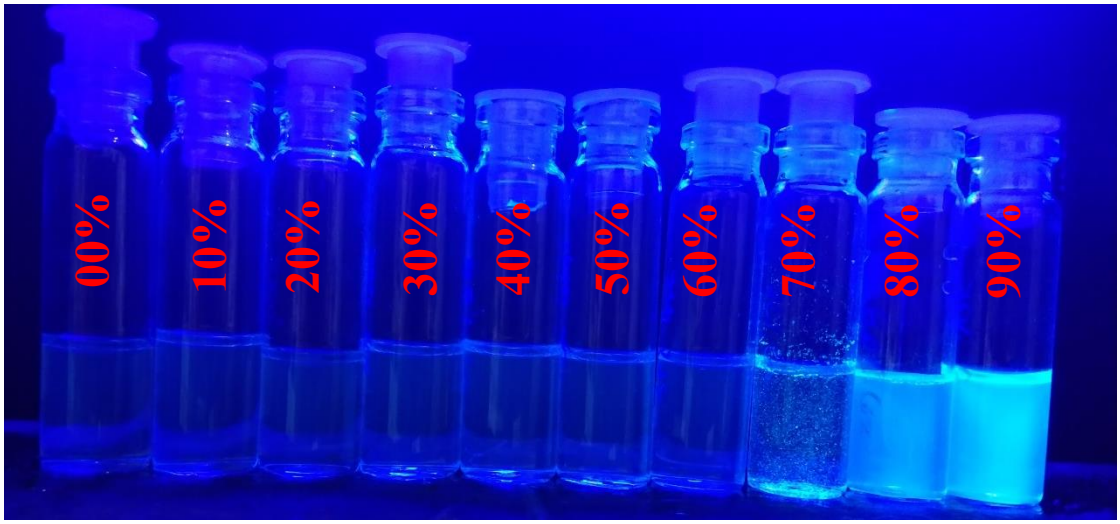


Fig. S27: Photograph of **SG** corresponding to different water fractions in THF under the UV irradiation of 365 nm.

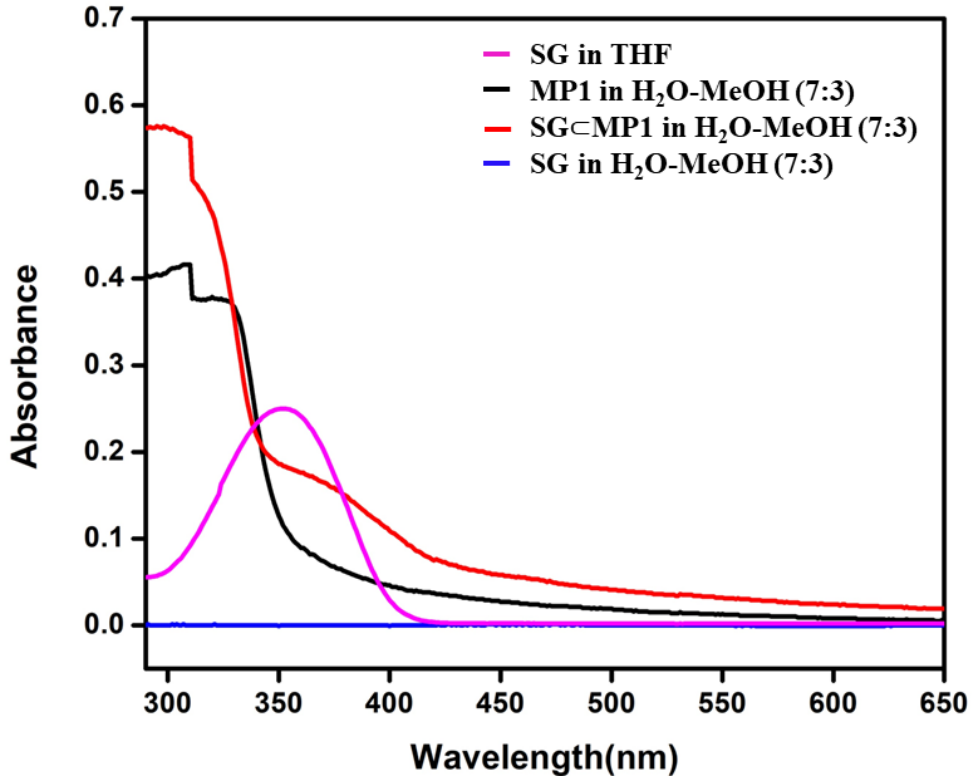


Fig. S28: UV-Vis spectra of **SG** in THF, **SG** in H_2O-MeOH (7:3), **MP1** in H_2O-MeOH (7:3), and **SG⊂MP1** in H_2O-MeOH (7:3) mixture.

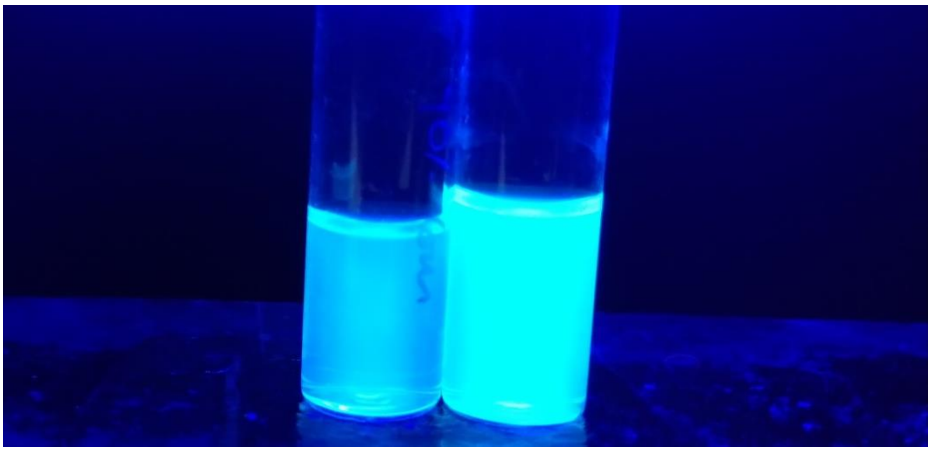


Fig. S29: Photograph of **SG** corresponding to its aggregated state in THF-water (1:9) (left) and **SG⊂MP1** in H_2O-MeOH (7:3) mixture (right) under the UV light of 365 nm.

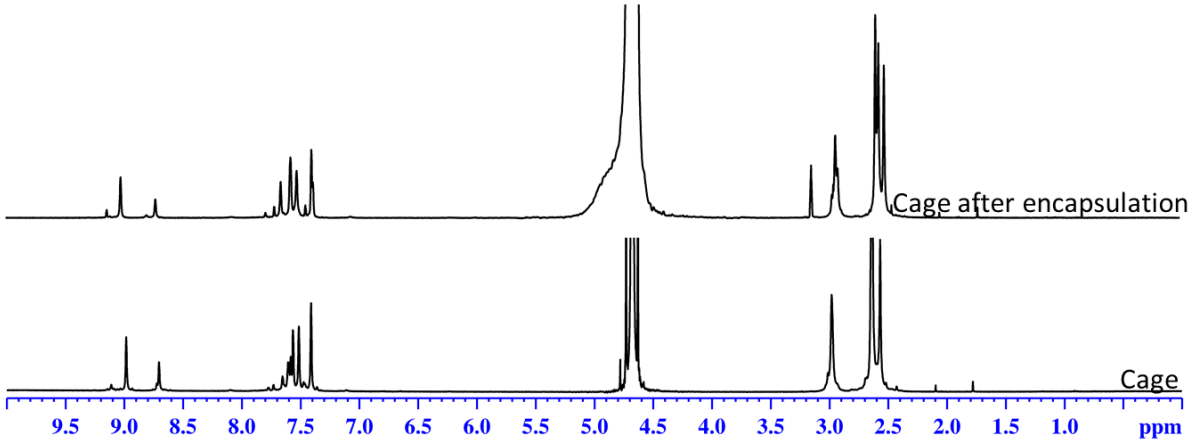


Fig. S30: Encapsulation study of the AIE active guest **SG** inside the nano-cavity of a molecular barrel[6] $[M_6L_4]^{12+}$, ^1H NMR of the barrel (bottom), and after the treatment of **SG** (top) in D_2O-CD_3OD (7:3) mixture.

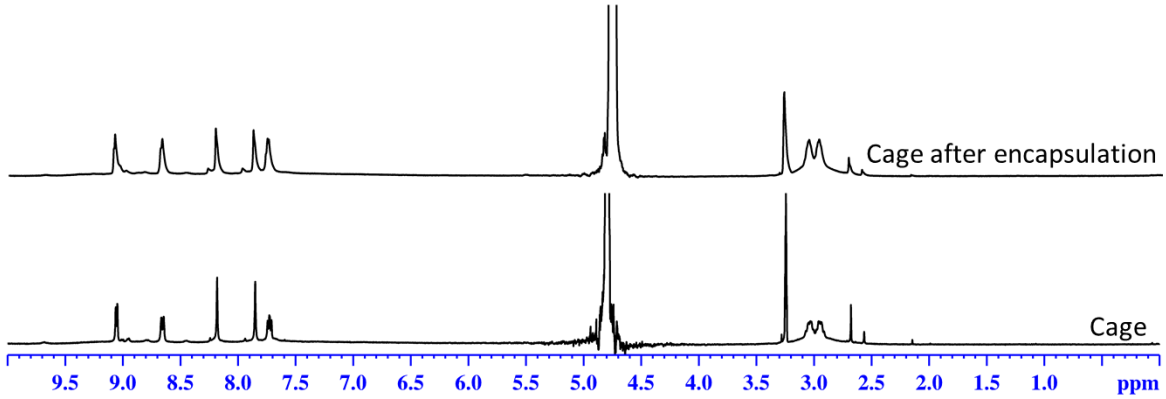


Fig. S31: Encapsulation study of the AIE active guest **SG** inside the nano-cavity of a trifacial molecular barrel[7] $[M_6L_3]^{12+}$, ^1H NMR of the barrel (bottom), and after the treatment of **SG** (top) in D_2O-CD_3OD (7:3) mixture.

Table S2: Absolute Fluorescence Quantum Yields of Compounds Under Different Conditions.

Systems	**Quantum Yields**
SG in THF	2.59%
SG in 90% H2O-THF mixture	48.02%
SG⊂MP1 in H_2O-MeOH (7:3) mixture	53.98%

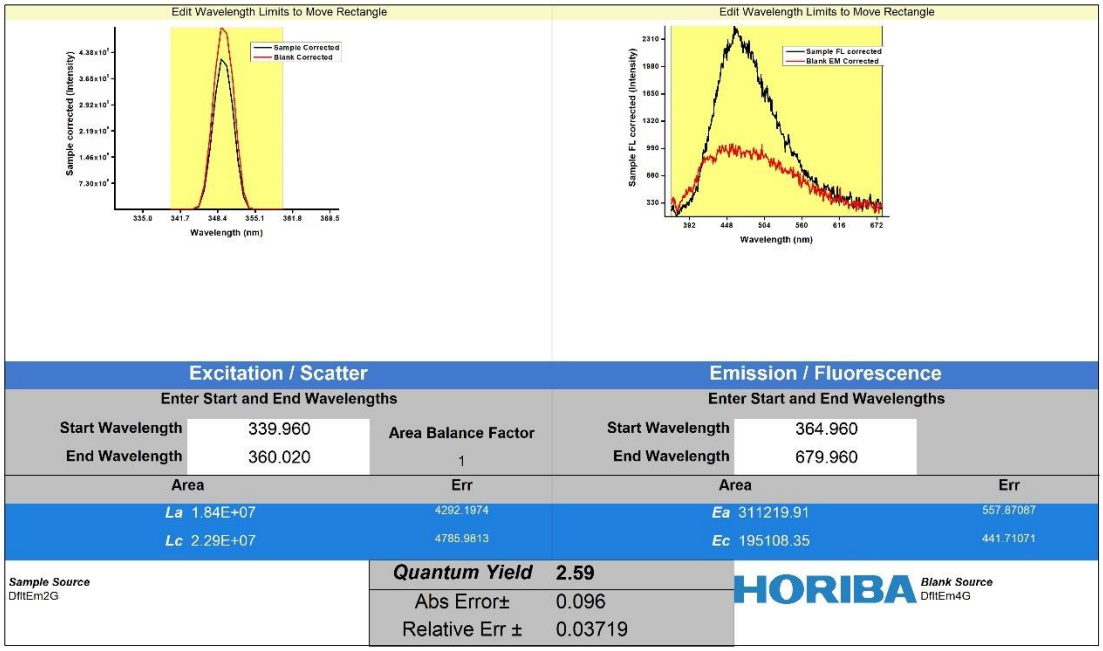


Fig. S32: Absolute fluorescence quantum yields of the **SG** {[**SG**] = 1.7 × 10^{-6} M} in THF (excitation/emission slit width: 2/2).

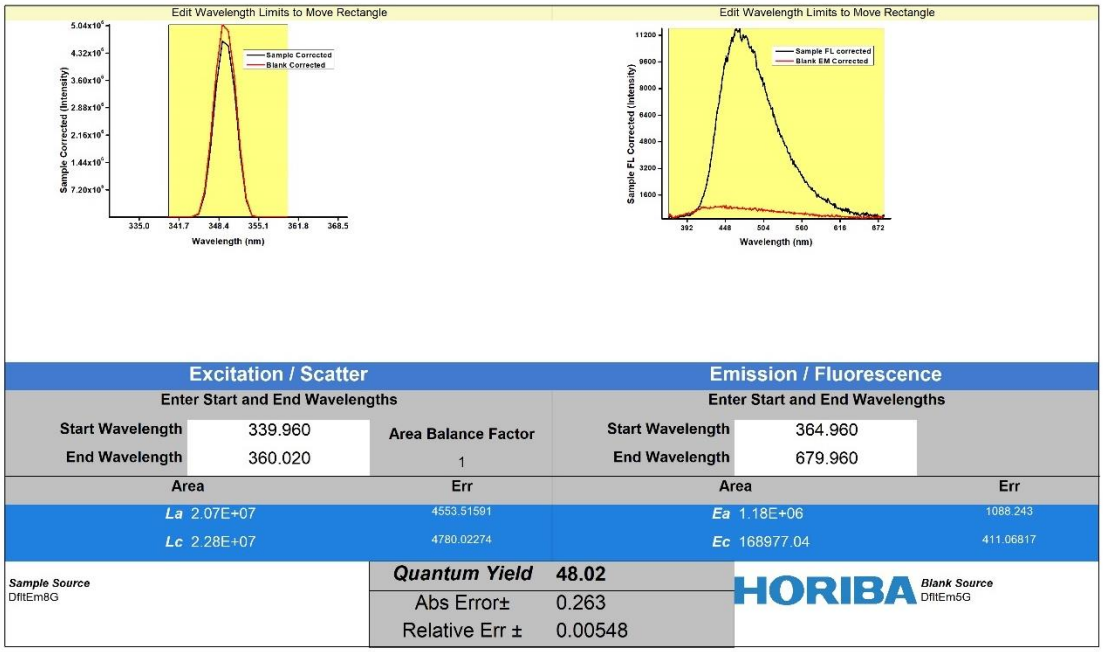


Fig. S33: Absolute fluorescence quantum yields of the **SG** {[**SG**] = 1.7 × 10^{-6} M} in 90% H_2O-THF mixture (excitation/emission slit width: 2/2).

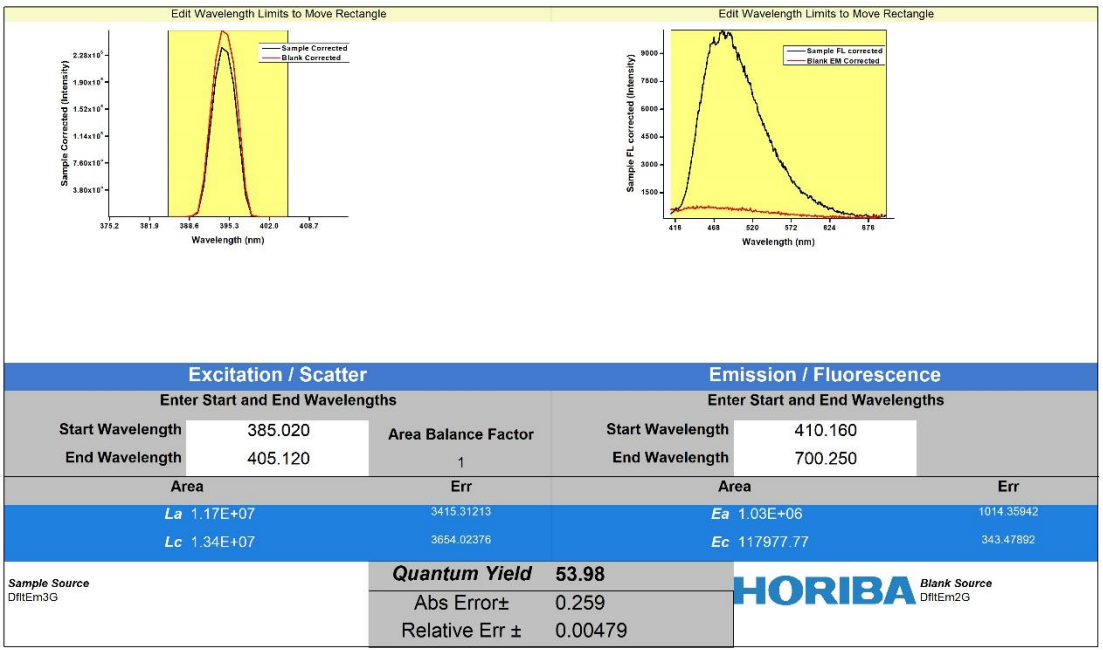


Fig. S34: Absolute fluorescence quantum yields of the **SG⊂MP1** in H_2O-MeOH (7:3) mixture {[**SG**] = 1.7×10^{-6} M} (excitation/emission slit width: 2/2).

References:

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Computed geometry for **SG⊂MP1:**

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symmetry c1

Pd	-8.807457000	-4.056785000	0.073799000
Pd	-7.854265000	4.095823000	-0.267008000
Pd	8.086843000	-5.045242000	-0.226610000
Pd	8.061667000	3.233591000	0.124436000
N	-7.406004000	-3.763720000	1.568581000
N	-7.338094000	-3.933068000	-1.375471000
N	-6.495597000	3.678285000	1.228518000
N	-6.488675000	3.498433000	-1.698565000
N	6.412353000	-4.780443000	0.957920000
N	7.032515000	-4.427869000	-1.904217000
N	6.994008000	2.619705000	1.796189000
N	6.342106000	3.000312000	-0.983335000
N	-5.277138000	-0.170501000	2.650634000
N	4.980392000	-1.146436000	2.592268000
N	-5.212534000	-0.469415000	-2.749474000
N	5.011064000	-0.639198000	-2.661343000
N	-10.365128000	-4.266594000	1.511408000
H	-10.301554000	-5.153907000	2.032043000
H	-10.409715000	-3.527002000	2.223939000
N	-10.299983000	-4.409385000	-1.397496000
H	-10.651640000	-3.542267000	-1.825825000
H	-10.033980000	-5.018845000	-2.182657000
N	-9.279090000	4.795109000	1.152447000
H	-9.451280000	4.168941000	1.949405000
H	-9.011631000	5.702446000	1.561404000
N	-9.291912000	4.586598000	-1.754246000
H	-8.933124000	5.032287000	-2.609255000
H	-9.832066000	3.770497000	-2.072266000
N	9.184834000	-5.748091000	1.447747000
H	9.534820000	-4.989111000	2.047988000
H	8.677793000	-6.388732000	2.073203000

N	9.853270000	-5.393718000	-1.365720000
H	9.788514000	-6.235405000	-1.957424000
H	10.131243000	-4.629735000	-1.994915000
N	9.864484000	3.506701000	1.218205000
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H	10.407373000	2.636618000	1.305654000
N	9.122063000	3.973577000	-1.555982000
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H	8.806459000	4.920667000	-1.812377000
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H	-7.895715000	-5.711595000	2.226066000
C	-6.445500000	-4.762416000	3.553475000
H	-6.407531000	-5.605990000	4.259924000
C	-5.653452000	-3.629341000	3.757834000
H	-5.001827000	-3.576777000	4.640963000
C	-5.706312000	-2.567626000	2.835366000
C	-7.155717000	-5.091551000	-2.080797000
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H	-6.149448000	-6.110219000	-3.716787000
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C	4.159803000	-4.763611000	2.626248000
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H	2.850036000	2.844783000	-2.703957000
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C	3.208280000	0.183502000	3.598162000
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H	11.188867000	4.698330000	-1.736730000
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H	-1.504479000	2.205778000	1.901169000
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C	2.923094000	9.504429000	-2.064328000
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H	1.017910000	9.654735000	-3.071551000
H	3.300724000	10.447193000	-2.475596000
C	1.789118000	5.601076000	1.013137000
C	1.528297000	6.593457000	1.973552000
C	2.414337000	4.405517000	1.401176000

C	1.879945000	6.384677000	3.309010000
H	1.061636000	7.536964000	1.672738000
C	2.765705000	4.203728000	2.739060000
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C	0.246674000	-1.505860000	-0.035032000
C	1.286032000	-0.650170000	0.361922000
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C	2.614773000	-0.994016000	0.101590000
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C	2.917623000	-2.197817000	-0.539363000
H	3.415315000	-0.324264000	0.409234000
H	2.114126000	-3.961992000	-1.502194000
H	3.953670000	-2.481553000	-0.701204000
C	-1.924950000	-2.443550000	0.726083000
C	-1.429947000	-3.287104000	1.736306000
C	-3.109810000	-2.784336000	0.058601000
C	-2.104531000	-4.466025000	2.058599000
H	-0.511148000	-3.024834000	2.262097000
C	-3.777247000	-3.970467000	0.381009000
H	-3.493980000	-2.134881000	-0.724707000
C	-3.275140000	-4.814725000	1.375091000
H	-1.710706000	-5.128469000	2.833342000
H	-4.679676000	-4.248434000	-0.158258000
H	-3.777755000	-5.754658000	1.608125000