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Supporting information for

Hydrophobicity Controls Guest Uptake Rh_8 Metallacages

Wei-Bin Yu*[a], Feng-Yi Qiu[a], Zhi-Feng Xin[a], and Sun Po[a]

Analysis and Testing Central Facility, Engineering Research Institute, Anhui University of Technology, Maanshan 243002, P. R. China.

E-mail:yuweibin@ahut.edu.cn

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1. General Methods

All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise mentioned. The starting material $[Cp^*RhCl_2]_2$ (Cp^*= η5- pentamethylcyclopentadienyl) was prepared by the literature method.[1] NMR spectra were recorded on Bruker AVANCE I 400 at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift δ H = 7.26 ($CDCl_3$), δ H = 3.31 (CD_3OD) are reported relative to the solvent residual peak. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were recorded on a Nicolet AVATAR-360IR spectrometer. UV spectra were recorded on a UV-VIS-NIR Spectrophotometer UV-3600 purchased from SHIMADZU in the range 185-3300 nm in solution.

2. Experimental Procedures

Synthesis of cage 1

AgOTf (25.7 mg, 0.1 mmol) was added to a solution of $[Cp^*RhCl_2]_2$ (62.0 mg, 0.1 mmol) in CH_3OH (10 mL) at room temperature. The reaction mixture was stirred in the dark for 6 h and then filtered, followed by addition of 4,4',4'',4'''-(1,2-ethenediylidenetetra-4,1-phenylene)tetrakis-Pyridine (EPTP), (32.0 mg, 0.05 mmol) and 2,5-Dichloro-3,6-Dihydroxy-*p*-Benzoquinone (20.8 mg, 0.1 mmol) with sodium hydroxide (8.0 mg, 0.2 mmol). After stirring for another 12 h at room temperature, the reaction mixture was concentrated to a volume of 3 mL under reduced pressure, filtered through celite and recrystallized by slow diffusion of diethyl ether into the filtrate. An brown crystalline solid (124.0 mg) was obtained in 78.0% yield. ^{1}H NMR (400 MHz, d_4-CD_3OD, ppm) δ = 8.35 (d, J = 8.0 Hz, 16H, pyridyl-ligand), 7.76 (d, J = 8.0 Hz, 16H, pyridyl-ligand), 7.51 (d, J = 8.0 Hz, 16H, phenyl-ligand), 7.17 (d, J = 8.0 Hz, 16H phenyl-ligand), 1.74 (s, 120H, methyl-Cp*); Elemental analysis calcd (%) for chemical formula: $C_{300}H_{184}Cl_8F_{24}N_8O_{40}Rh_8S_8$: C, 56.66; H, 2.92; N, 1.76; Found: C, 56.45; H, 2.84; N, 1.71. IR (KBr cm^{-1}): 3474, 3461, 2920, 1611, 1494, 1370, 1256, 1158, 1075, 1028, 854, 822, 752, 638.

Guest uptake and binding constants (*K*) test

The guests (0.005 mmol for **G2**, 0.003 mmol for **G2**, 0.005 mmol for **G3**) and the cage (0.001 mmol) were mixed into NMR tube CD_3OD, treated in ultrasonic instrument for some time. Their processes of uptake guests in host were monitered by ^{1}H NMR every several minutes. According to the results detected by ^{1}H NMR, the *K* values was calculated by the following equations:[2]

$$1 + G \overset{K}{\rightleftharpoons} G \subset 1 \qquad (1)$$

$$K = \frac{[G \subset 1]}{([1]-[G \subset 1])([G]-[G \subset 1])} \qquad (2)$$

3. NMR Specta

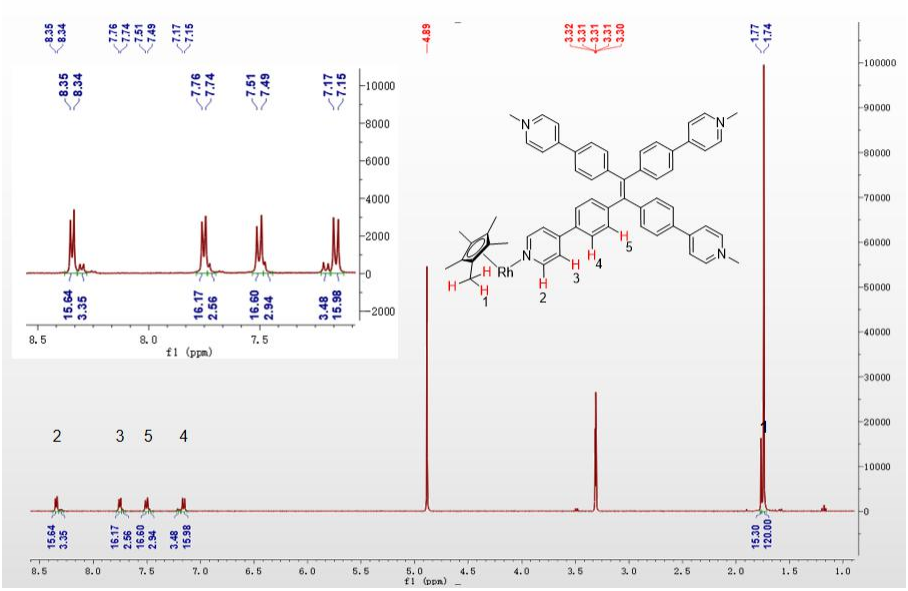

Fig. s1. ^{1}H NMR spectrum of **1** in CD_3OD.

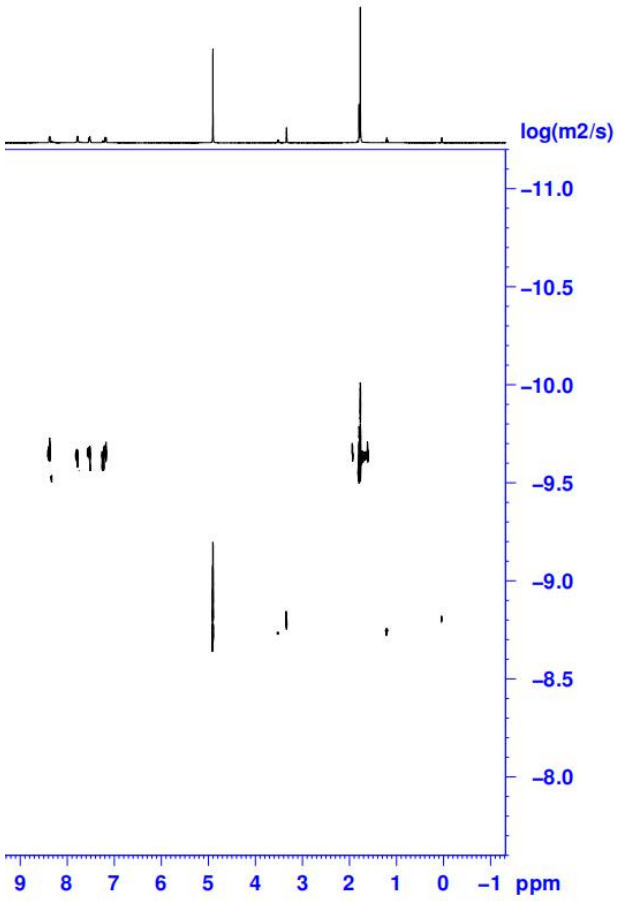

Fig. s2. ^{1}H-^{1}H DOSY NMR spectrum of **1** in CD_3OD.

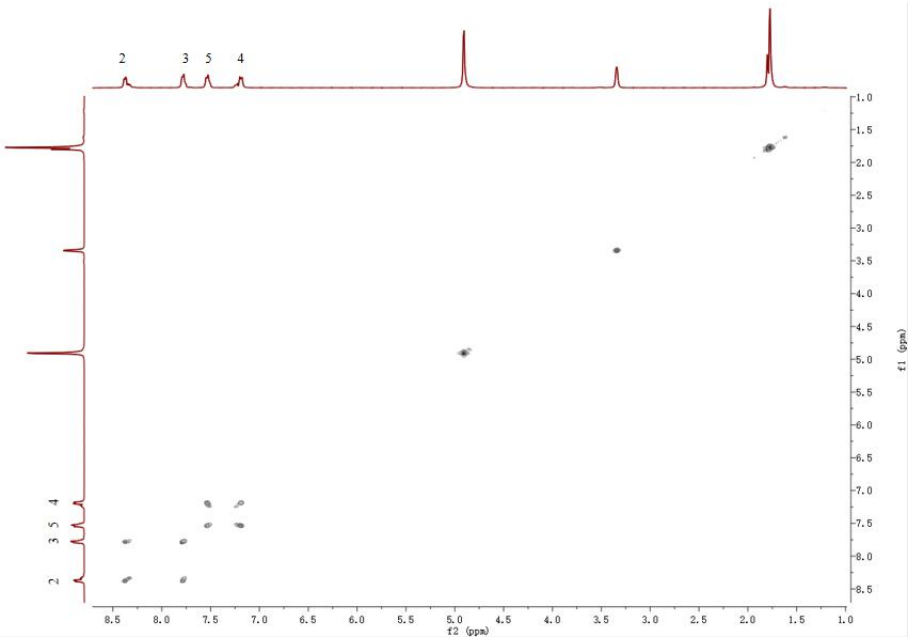

Fig. s3. 2D ^{1}H-^{1}H COSY NMR spectrum of **1** in CD_3OD.

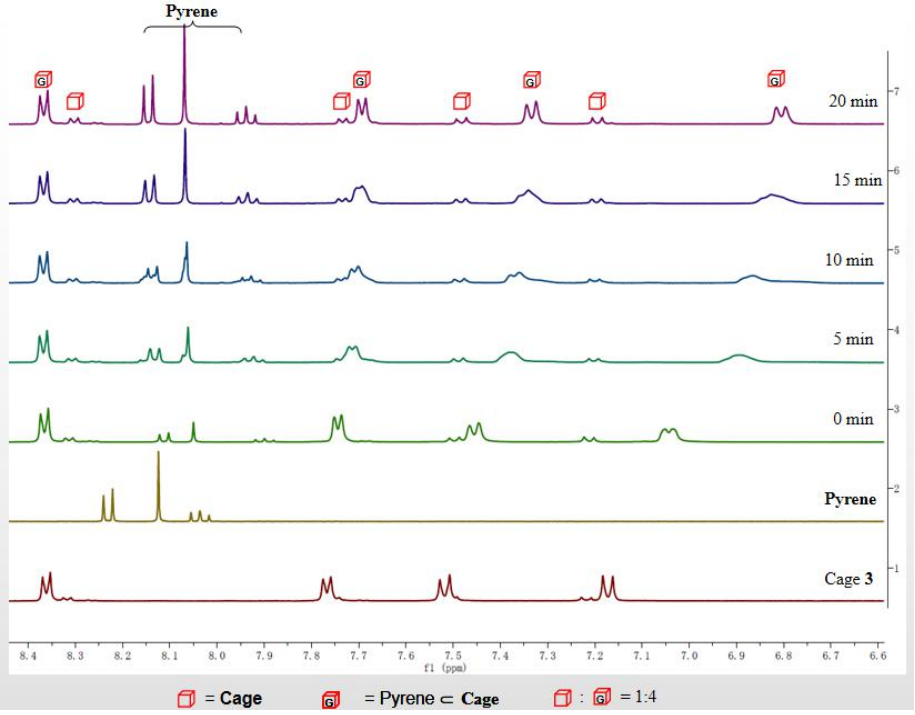

Fig. s4. Self-assembly processes of Pyrene-encapsulating Cage **1** determined by ^{1}H NMR.

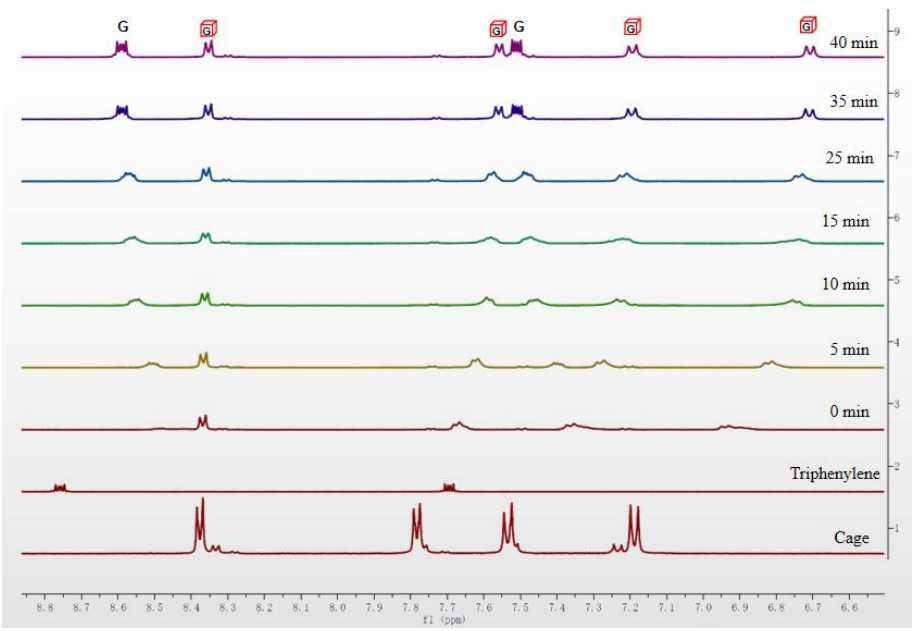

Fig. s5. Self-assembly processes of triphenylene-encapsulating Cage **1** determined by ^{1}H NMR.

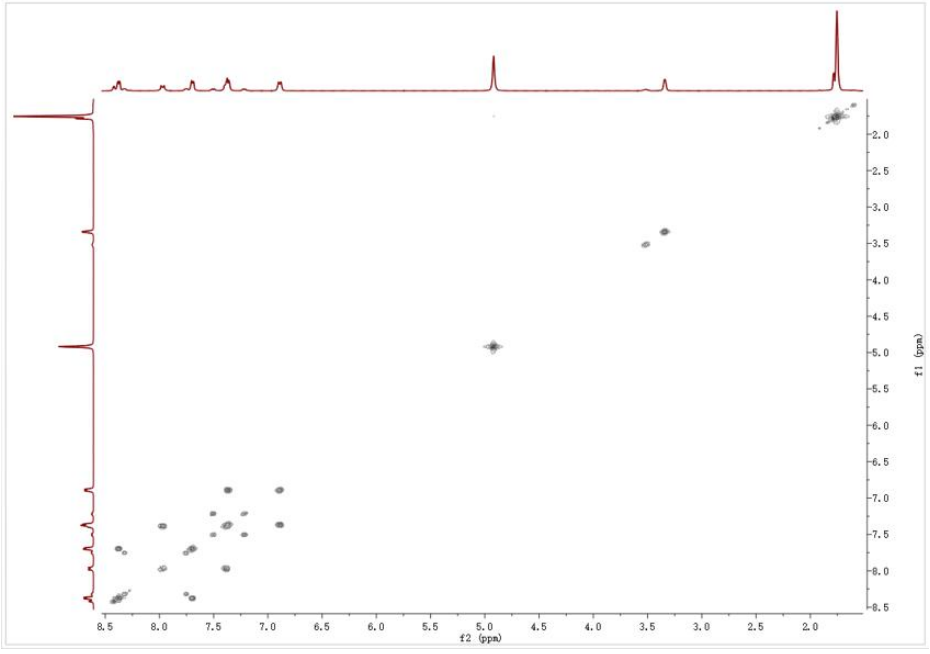

Fig. s6. ^{1}H-^{1}H 2D COSY NMR spectra of Anthracene-encapsulating Cage **1**.

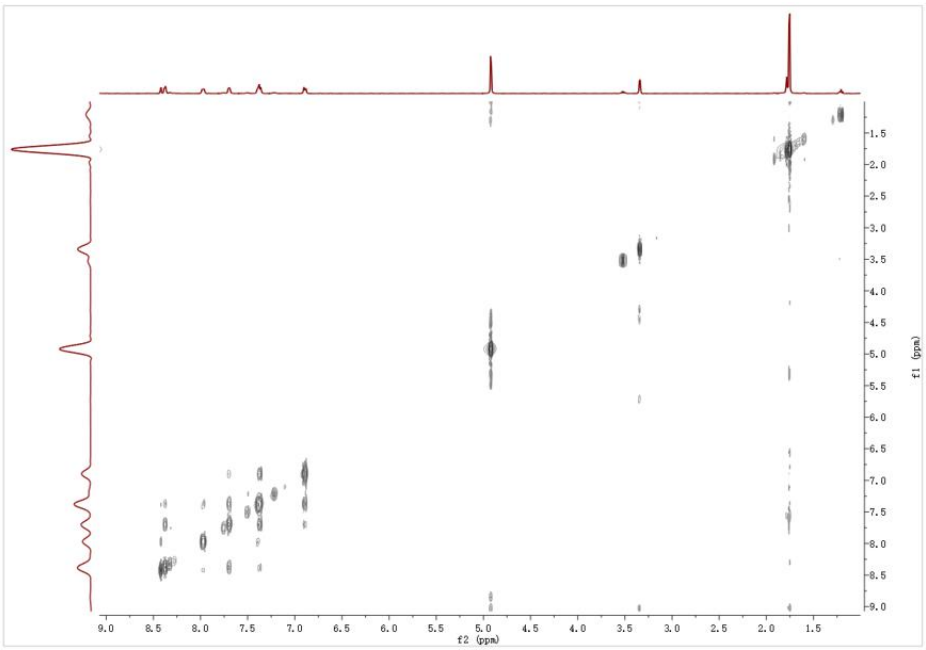

Fig. s7. ^{1}H-^{1}H 2D NOESY NMR spectra of Anthracene-encapsulating Cage **1**.

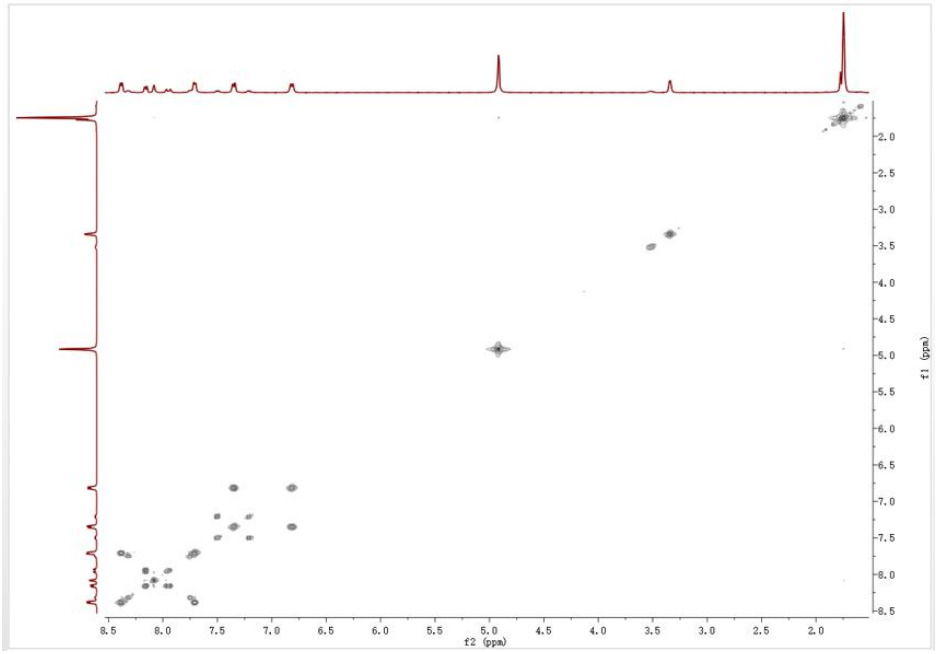

Fig. s8. ^{1}H-^{1}H 2D COSY NMR spectra of Pyrene-encapsulating Cage **1**.

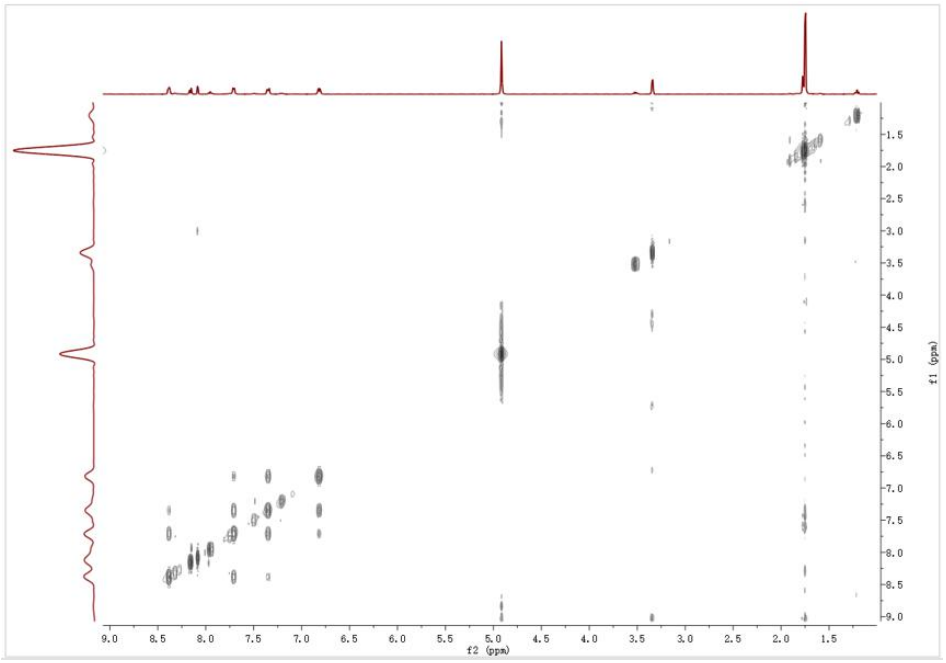

Fig. s9. ^{1}H-^{1}H 2D NOESY NMR spectra of Pyrene-encapsulating Cage **1**.

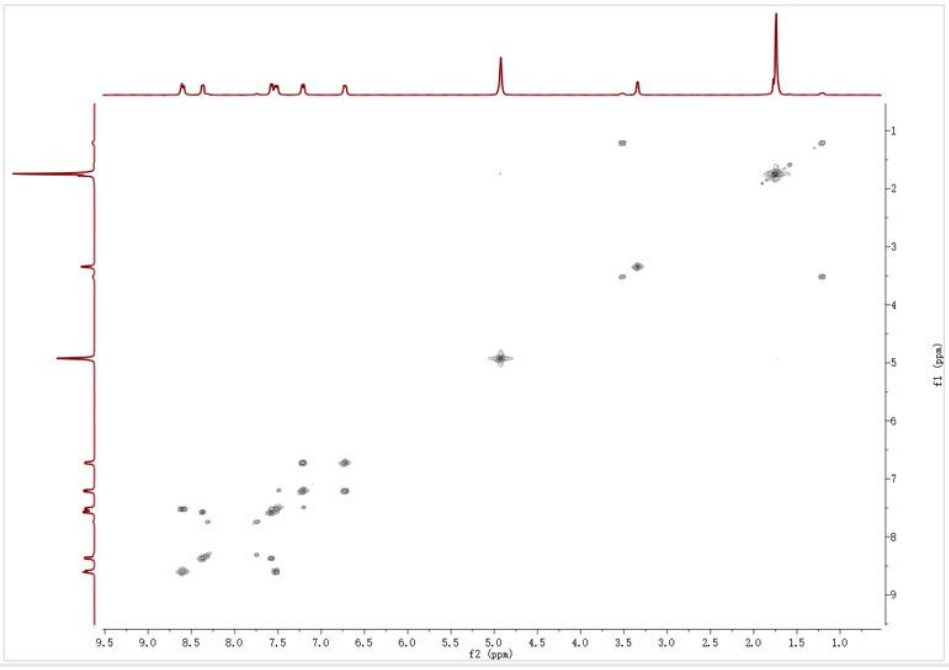

Fig. s10. ^{1}H-^{1}H 2D COSY NMR spectra of Triphenylene-encapsulating Cage **1**.

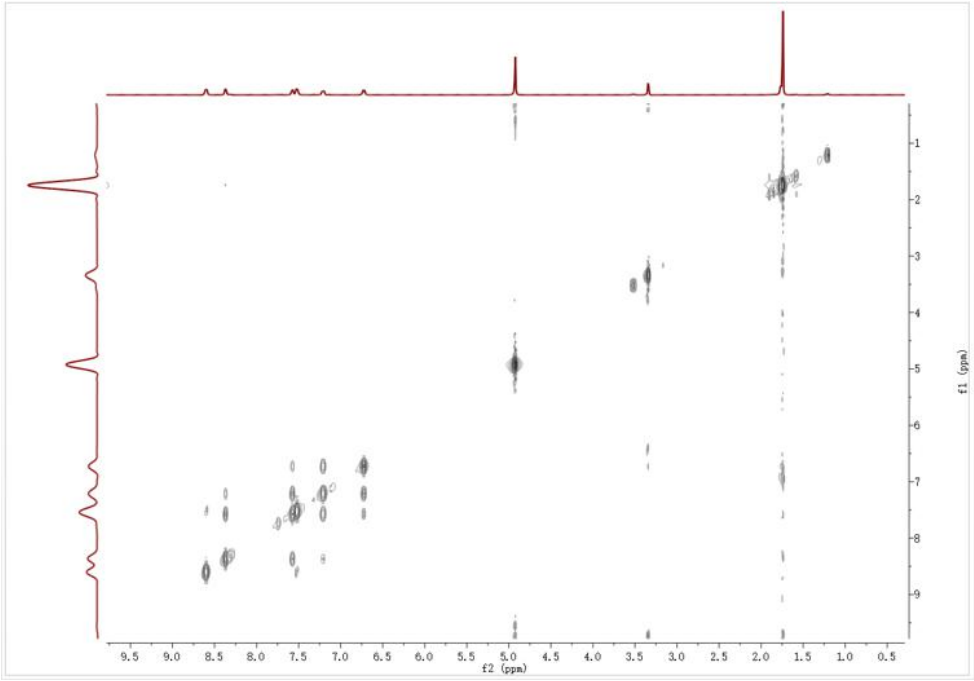

Fig. s11. ^{1}H-^{1}H 2D NOESY NMR spectra of Triphenylene-encapsulating Cage **1**.

4.X-Ray Crystallographic Details

Table s1. Crystal data of **1**.

	Cage **1**
Formula	
M_r	5204.93
T [K]	193
Crystal system	triclinic
Space group	P-1
a [Å]	16.8448(18)
b [Å]	18.457(2)
c [Å]	25.850(3)
α [°]	96.150(5)
β [°]	102.186(5)
γ [°]	99.661(5)
V [Å^3]	7659.5(15)
Z	1
ρ_{calcd} [g cm^{-3}]	1.128
F(000)	2622
Crystal size [mm^3]	0.180 × 0.160 × 0.140
$2\theta_{max}$ [°]	57.14
Reflections collected	29485
Independent reflections	18737
Parameters	1370
R_1 [$I > 2\sigma(I)$]	0.1765
wR_2 [all data]	0.2590
GOF	1.027
CCDC number	1962384

5.References

1 C. White, A.Yates, P. M. Maitlis, D. M. Heinekey, *Inorg. Synth.*1992, **29**, 228−234.

2 (a)L. Fielding,*Tetrahedron* 2000, **56**, 6151-6170. (b)Y. Kikuchi, Y. Kato, Y. Tanaka, H. Toi and Y. Aoyama, *J. Am. Chem. Soc.* 1991, **113**, 1349-1354.