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Electronic Supplementary Information

A newly supramolecular catalytic system: the supramolecular self-assembly of Rh8 cages host anthracene molecules for [4+4] cycloaddition induced by UV irradiation

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I. Materials and 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.

II. 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 sodium oxalate (13.4 mg, 0.1 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 (106.0 mg) was obtained in 72.0% yield. ^{1}H NMR (400 MHz, d_4-CD_3OD, ppm) δ = 8.21 (d, J = 8.0 Hz, 16H, pyridyl-ligand), 7.75 (d, J = 8.0 Hz, 16H, pyridyl-ligand), 7.41 (d, J = 12.0 Hz, 16H, phenyl-ligand), 7.21 (d, J = 8.0 Hz, 16H phenyl-ligand), 1.66 (s, 120H, methyl-Cp*); Elemental analysis calcd (%) for chemical formula: $C_{284}H_{184}F_{24}N_8O_{40}Rh_8S_8$: C, 57.97; H, 3.15; N, 1.90; Found: C, 57.38; H, 3.10; N, 1.82. IR (KBr cm^{-1}): 3451, 1635, 1488, 1449, 1401, 1384, 1354, 1256, 1224, 1159, 1068, 1031, 908, 818, 741, 638.

Guest uptake

The guest (0.005 mmol for ANT) 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.

III. Supplemental Figures

a. NMR data

a

Fig. s1. a) ^{1}H NMR (400 MHz, CD_3OD, ppm) and b) DOSY spectrum for **1**.

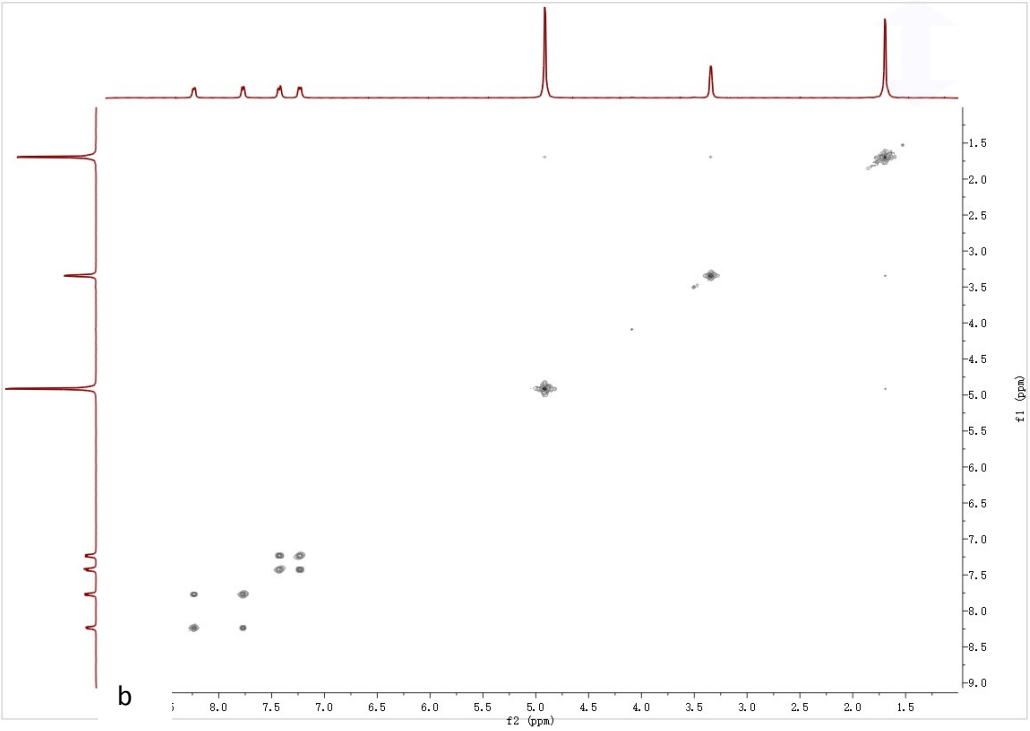

Fig. s2. 2D-^{1}H,^{1}H NMR-COSY (400 MHz, CD_3OD, ppm) for **1**.

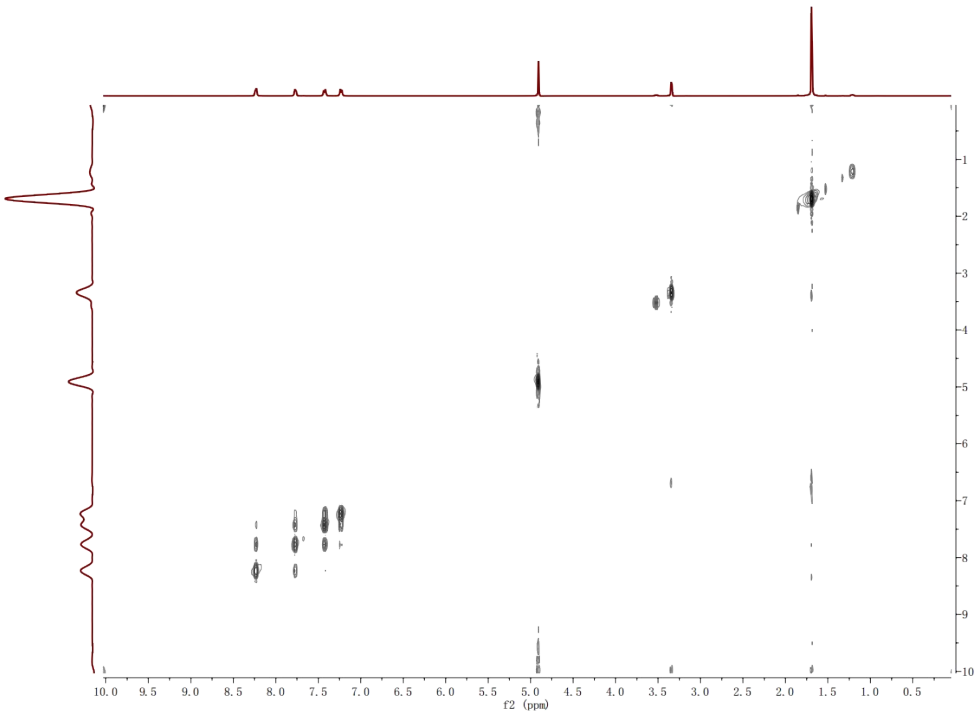

Fig. s3. 2D-^{1}H,^{1}H NMR-NOESY (400 MHz, CD_3OD, ppm) for **1**.

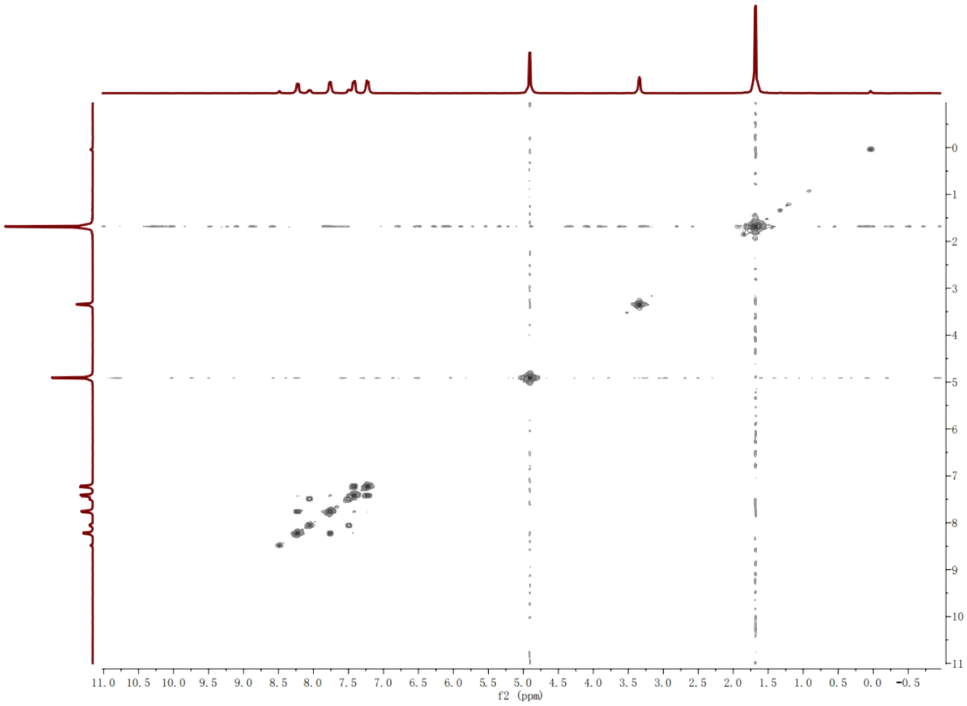

Fig. s4. 2D-^{1}H,^{1}H NMR-COSY (400 MHz, CD_3OD, ppm) for ANT@**1**.

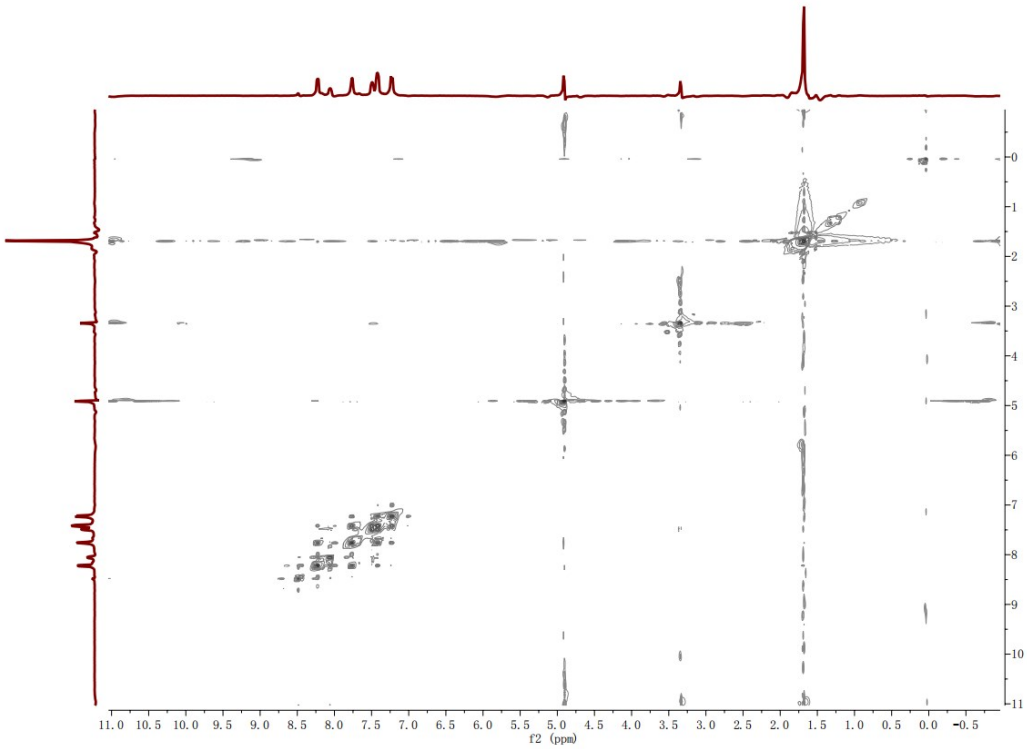

Fig. s5. 2D-^{1}H,^{1}H NMR-NOESY (400 MHz, CD_3OD, ppm) for ANT@**1**.

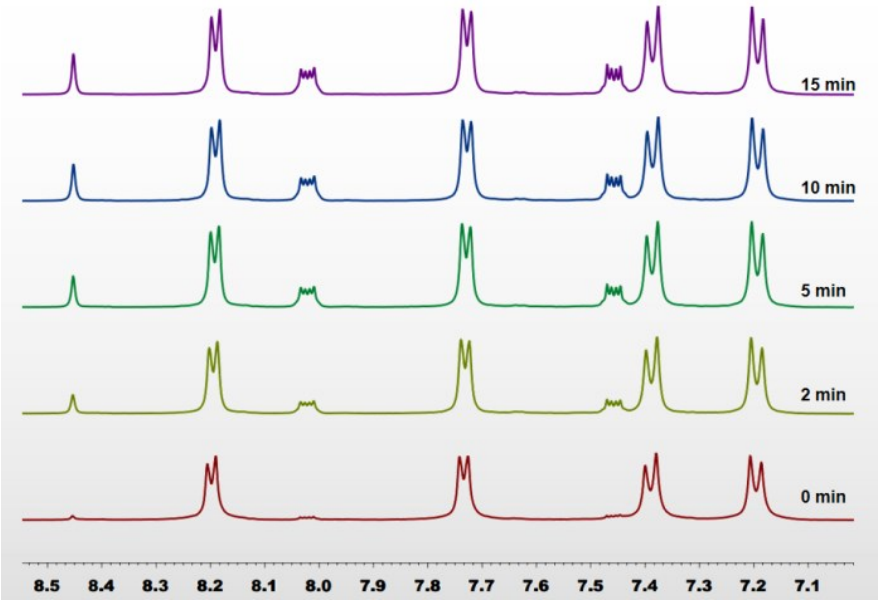

Fig. S6. The procedure of guest ANT uptake for the cuboid **1** monitored by ^{1}H NMR in MeOD-D_4.

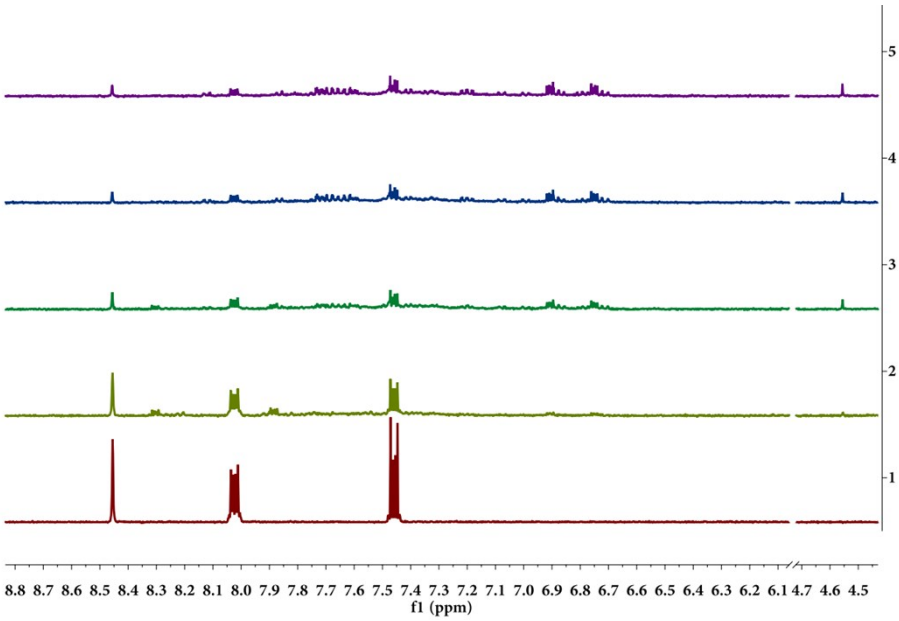

Fig. S7. The photocycloaddition reaction of ANT in the absence of cuboid **1** monitored by ^{1}H NMR in MeOD-D_4.

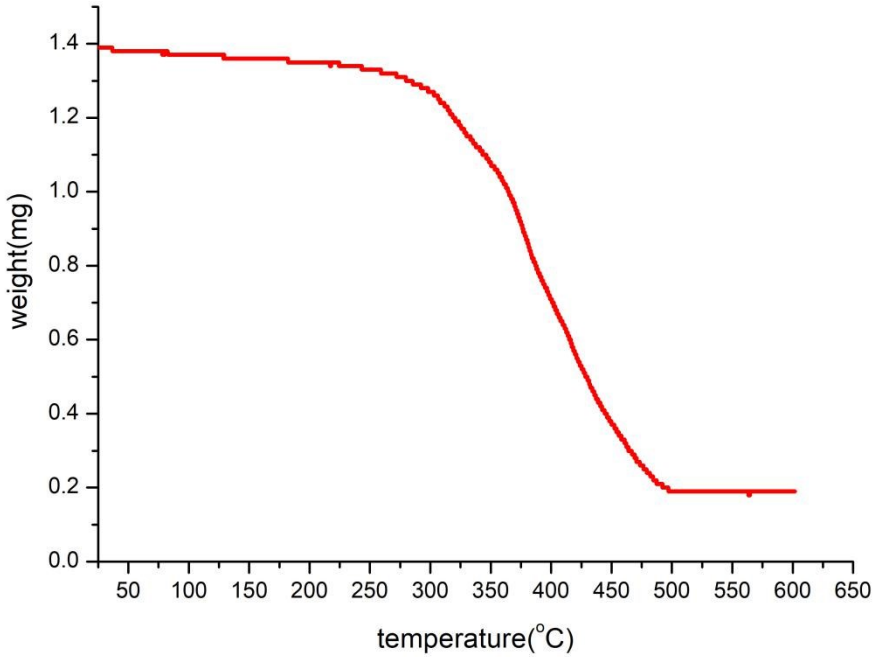

Fig. S8. TGA curve of **1**.

b. X-Ray Crystallographic Details

Tab.s1. crystal data of cage **1**.

	Cage **1**
Formula	$C_{188}H_{183}F_{24}N_8O_{40}Rh_8S_8$
M_r	4730.17
T [K]	193
Crystal system	triclinic
Space group	P-1
a [Å]	16.3634(13)
b [Å]	22.2895(17)
c [Å]	38.292(3)
α [°]	103.235(3)
β [°]	91.953(3)
γ [°]	109.093(3)
V [Å^3]	12757.0(17)
Z	2
ρ_{calcd} [g cm^{-3}]	1.231
F(000)	4782
Crystal size [mm^3]	0.500 × 0.210 × 0.210
$2\theta_{max}$ [°]	57.38
Reflections collected	52335
Independent reflections	6191
Parameters	2524
R_1 [$I > 2\sigma(I)$]	0.0805

wR_2 [all data]	0.2261
GOF	1.090
CCDC number	1974908

IV. References

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