Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for

Size recognition and optical unloading of polyaromatic compounds based on coordination box contain face-to-face olefin bonds

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S1

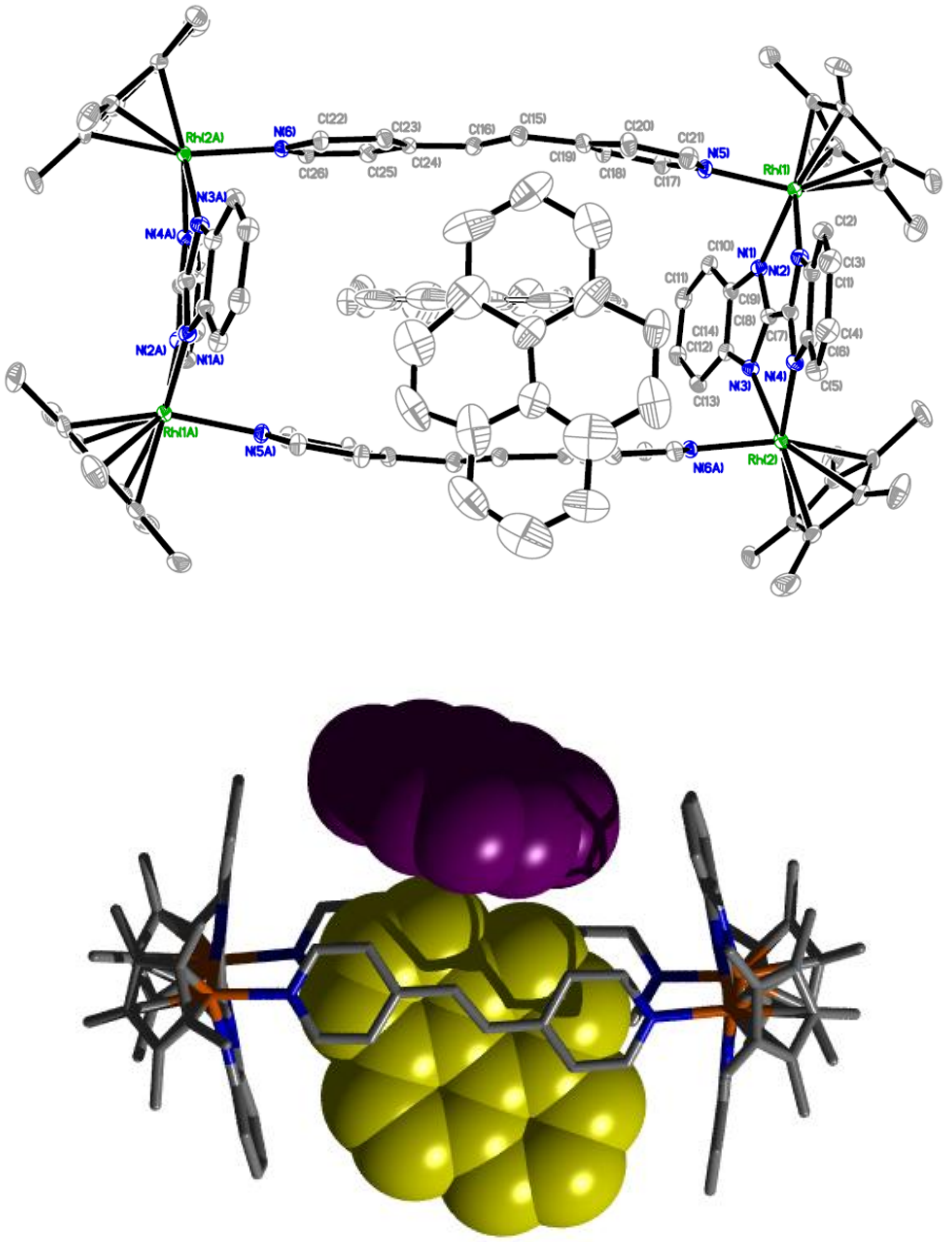


Fig. S1 (a) Cation structure of **4** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. (b) Top view of the Cation **4.** Selected distances (Å) and angles (°): Rh(1)-N(5) 2.119(3), Rh(1)-N(1) 2.160(4), Rh(1)-N(2) 2.204(3), C(15)-C(16) 1.333(6), C(16)-C(19) 1.464(5), N(5)-Rh(1)-N(1) 89.25(13), N(5)-Rh(1)-N(2) 88.57(12), N(1)-Rh(1)-N(2) 79.55(12), C(16)-C(15)-C(19) 125.0(4).

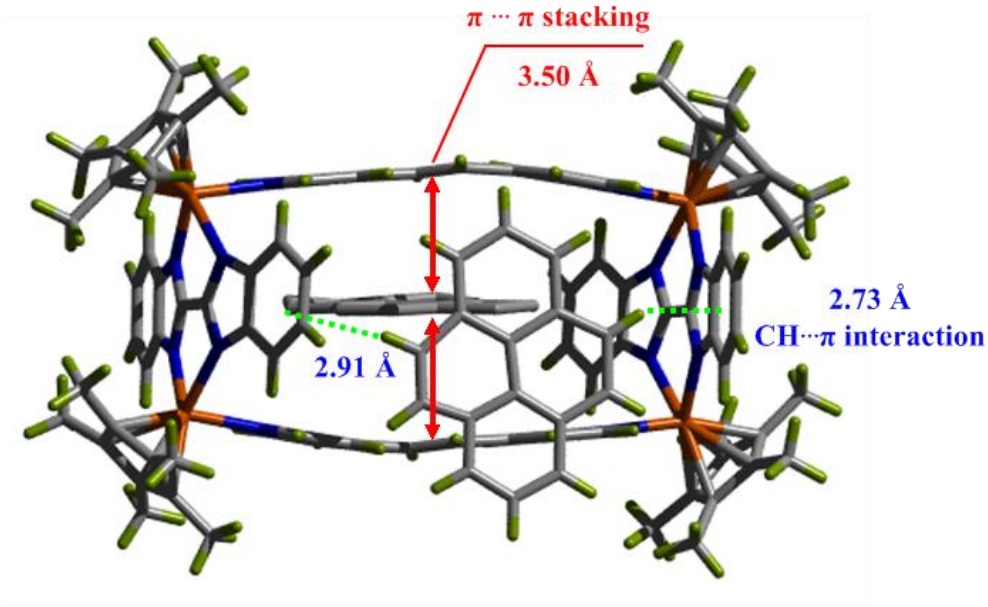


Fig. S2 Intramolecular action between the host and the guests.

One is clipped by two olefin double bond mainly contributed by π ··· π stacking interaction like the pyrene-1-carboxaldehyde we mentioned in the context. Another one is just vertical to this pyrene, and insert in the two wings of 2,2'-bisbenzimidazole ligands. What make it solidly keep in the cavity of the host are the CH ···π interaction occurred on the two sites of the pyrene.

S3

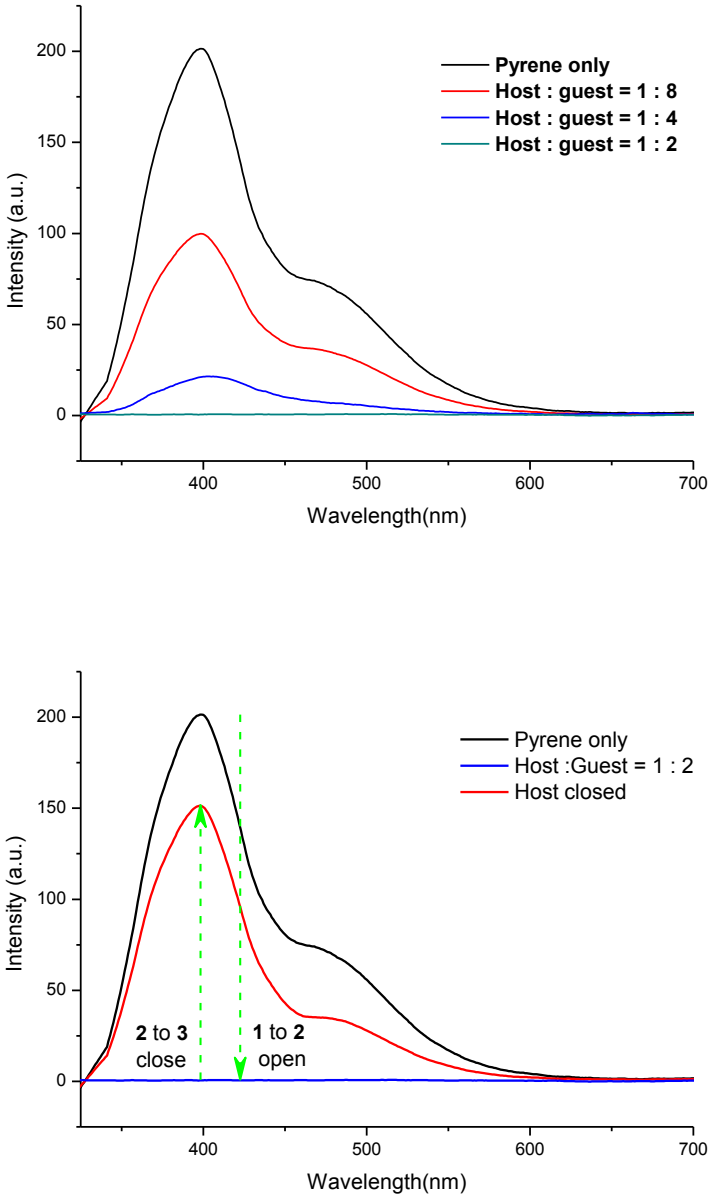


Fig. S3 Up: Fluorescence-emission control variable of pyrene by metallarectangle **1** (excitation wavelength 300 nm); down: Intensity of fluorescence emission falls down in the process of structure opening, and recovers in the process of structure closing.

As shown in fig. S3, we can get information that the fluorescence emission can be thoroughly quenched only until the ratio of host to guest is 0.5. This coincides with what the cation **4** showed us that one host molecular can encapsulate two pyrene molecules.

S4-1

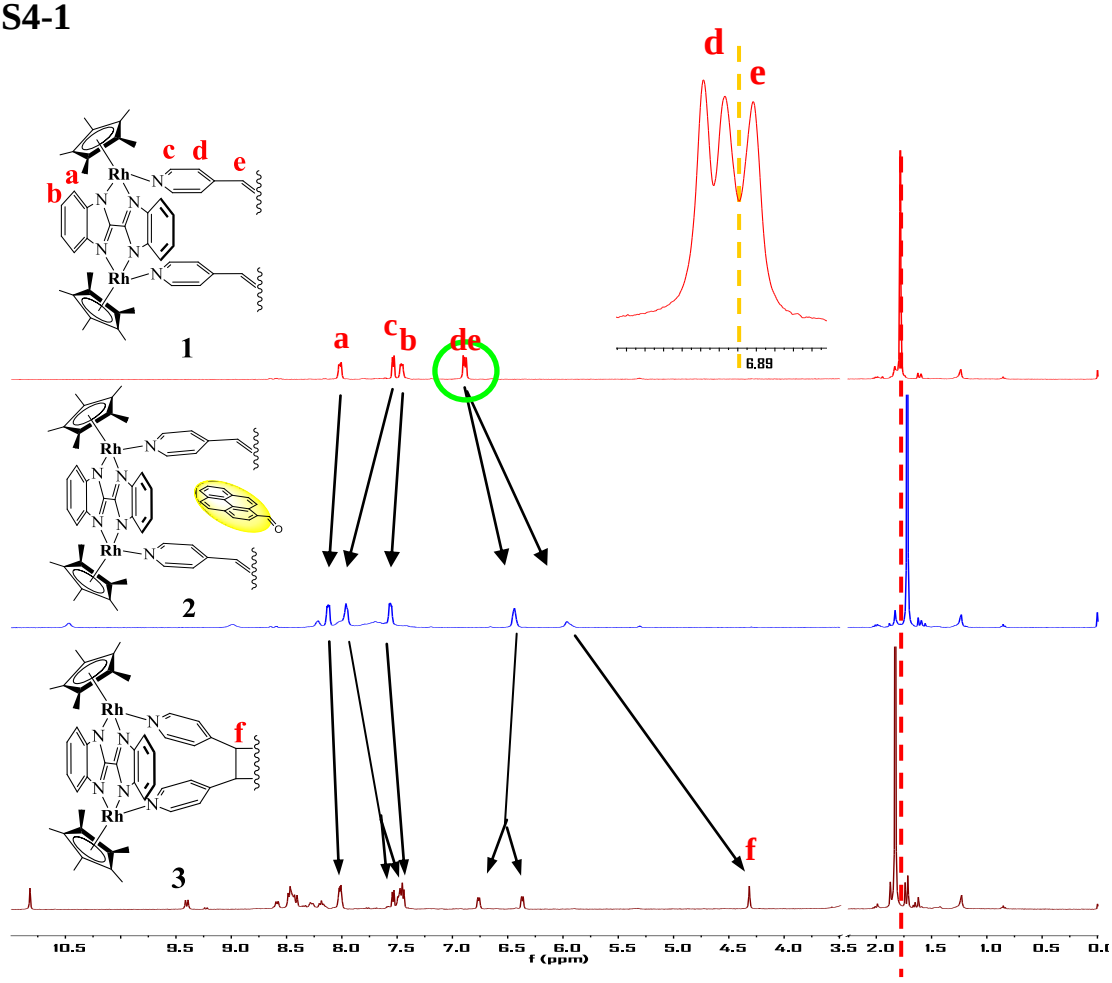


Fig. S4-1 NMR spectroscopy. Up: only complex **1** in the DMSO(solution **A**); middle: after adding pyrene-1-carboxaldehyde into **A** for 5 minutes(solution **B**); down: after irradiation on **B** under UV light(365nm) for 16 hours(solution **C**).

S4-2

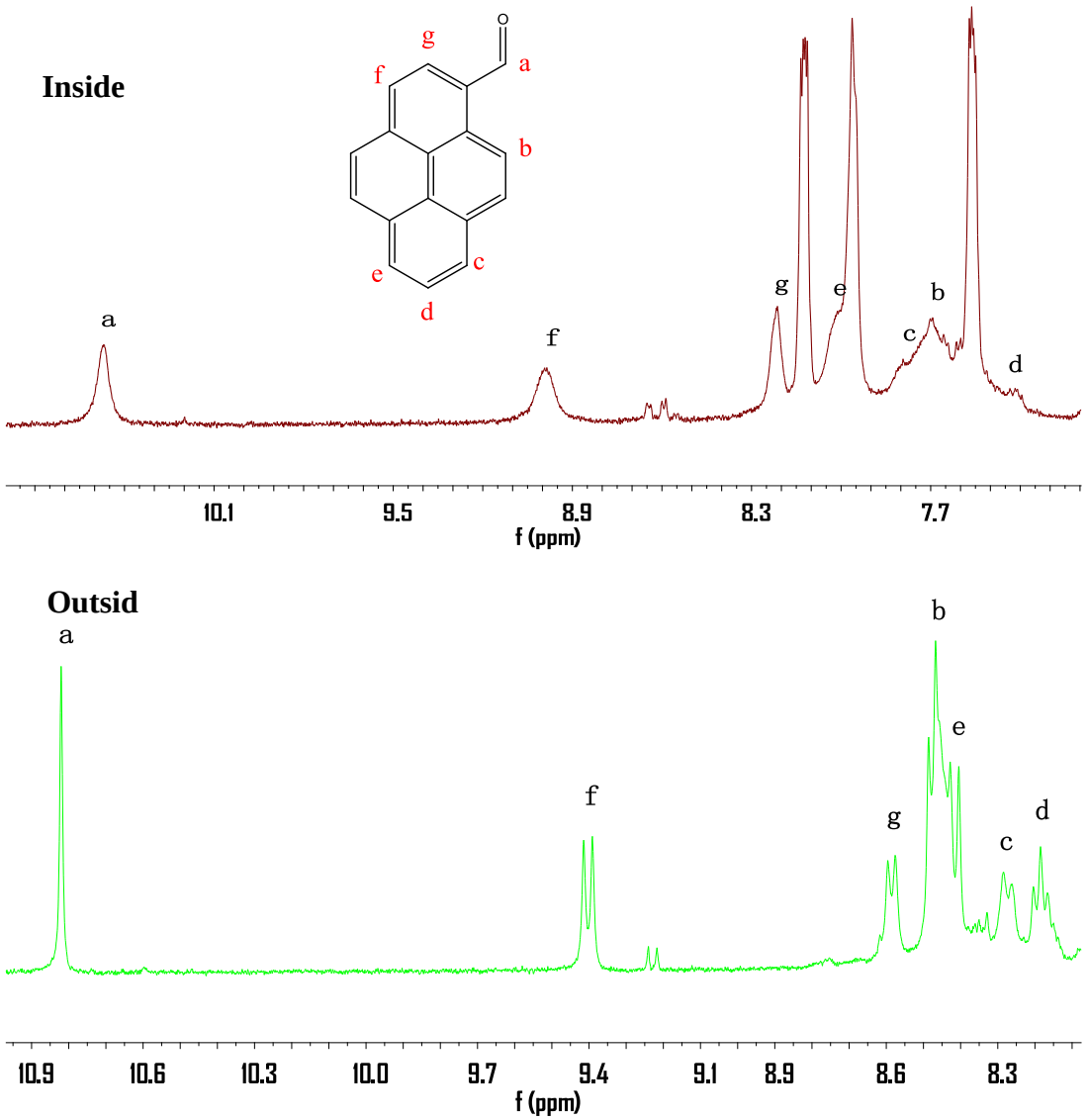


Fig. S4-2 NMR spectroscopy. Up: low field of solution B; down: low field of solution C.

S5 ^{1}H NMR titration experiments:

To determine the association constants (K_a) for complex **1** binding with Pyrene-1-carboxaldehyde, ^{1}H NMR titration experiments were done with $CDCl_3$ solutions which had a constant concentration of complex **1** (4.0 mM) and varying concentration of guest. From the crystal structure of cation **2**, a 1:1 stoichiometry was obtained for complex **2**. The association constants (K_a) of them were estimated by a non-linear curve-fitting method with the equation:[1]

$$\Delta\delta = (\Delta\delta_\infty/[H])\{0.5([G]+[H]+1/K_a)-0.5(([G]+[H]+1/K_a)^2-4[H][G])^{0.5}\} \quad \text{Eq. 1}$$

Where $\Delta\delta$ is the chemical shift change of pyridyl-H (close to the ethenyl) on compelx **1** at [G], $\Delta\delta_\infty$ is the chemical shift change of pyridyl-H (close to the ethenyl) when compelx **2** is completely formed, [H] is the fixed initial concentration of the host, and [G] is the concentration of Pyrene-1-carboxaldehyde.

From the crystal structure of cation **4**, a 1:2 stoichiometry was obtained for complex **1** with pyrene. The association constant (Ka) should be estimated by a non-linear curve-fitting method with the equation:[1]

$$\Delta\delta = (\Delta\delta_{HG}K_1[G]+\Delta\delta_{HG2}K_1K_2[G]^2)/(1+K_1[G]+K_1K_2[G]^2) \quad \text{Eq. 2}$$

But actually from the molar ratio plot based on the chemical shift change of pyridyl-H (close to the ethenyl), a 1:1 stoichiometry was obtained for complex **4.** That because the second pyrene was catched by the two pacers of the macrocycle far from the ethenyl. Hydrogen bond and CH···π interaction are the main contributions to reserve the second pyrene. So there's almost no effect to make any shift of the hydrogen around the reaction center. Therefore, the equation 1 was also used to get the association constant (K_a) for complex **4**.

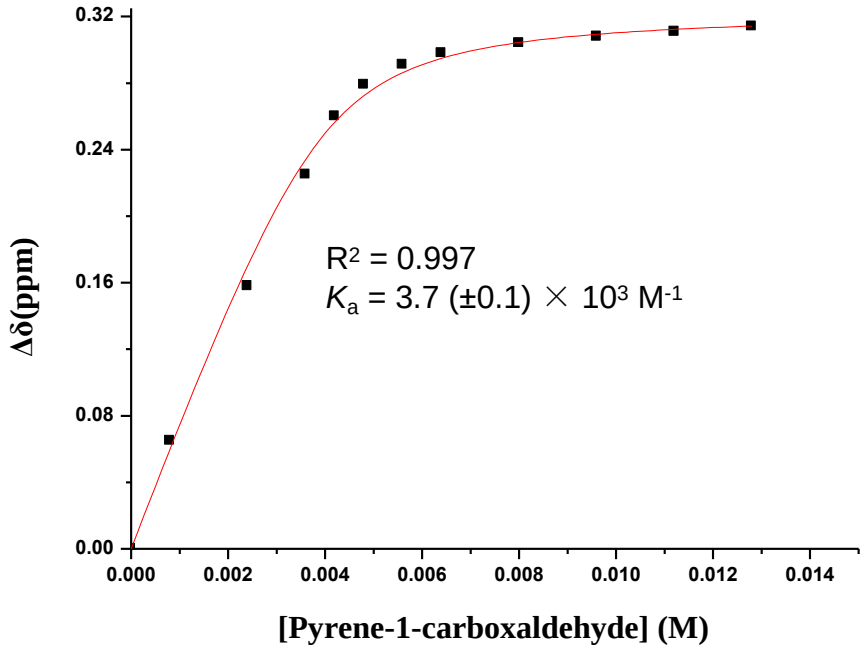


Fig. S5-1 Changes of the chemical shift changes of pyridyl-H (close to the ethenyl) on compelx **1** with addition of Pyrene-1-carboxaldehyde. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

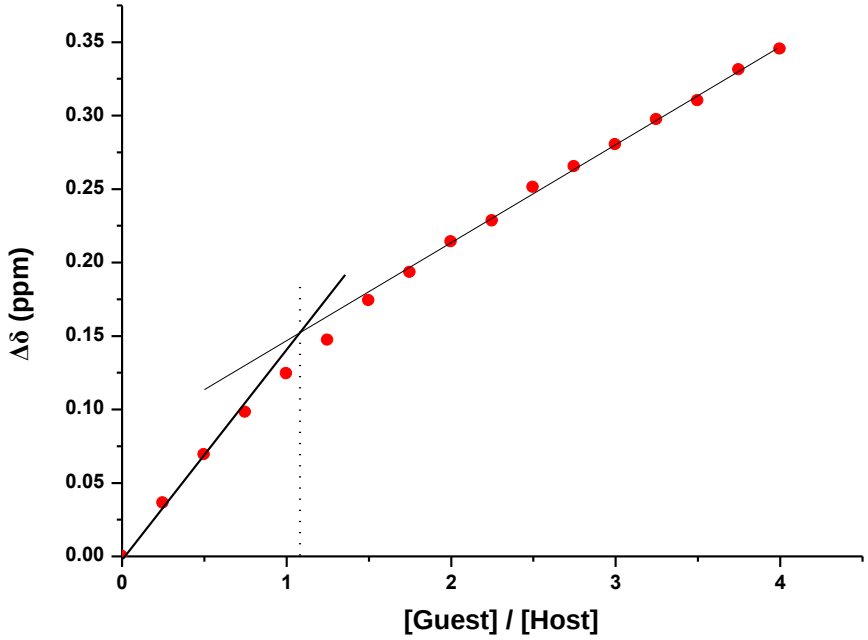


Figure S5-2. Molar ratio plot for the binding of pyrene with complex **1** in DMSO-d at 25 °C.

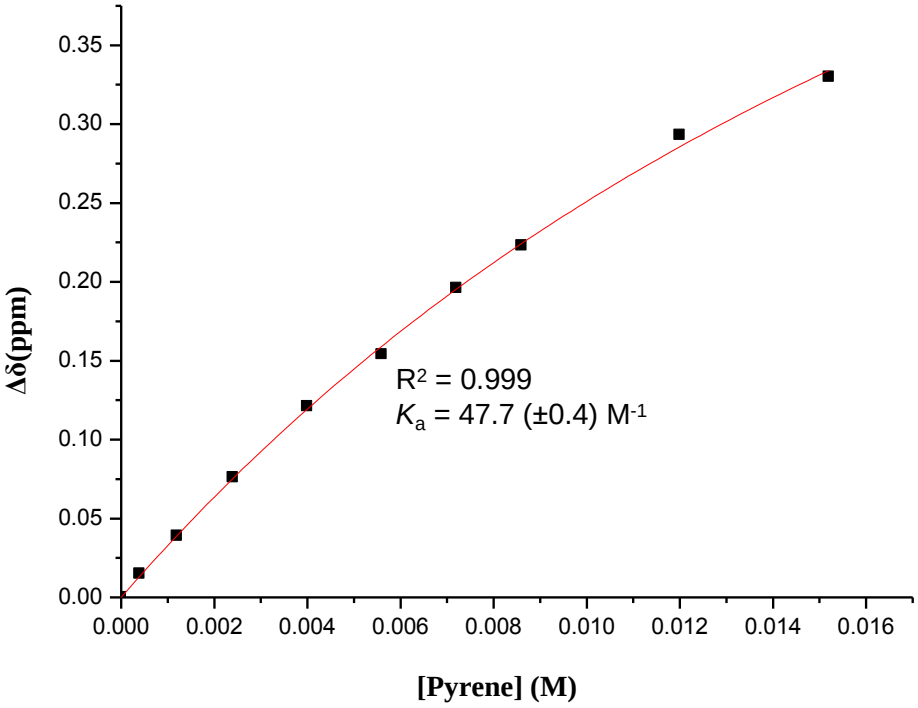
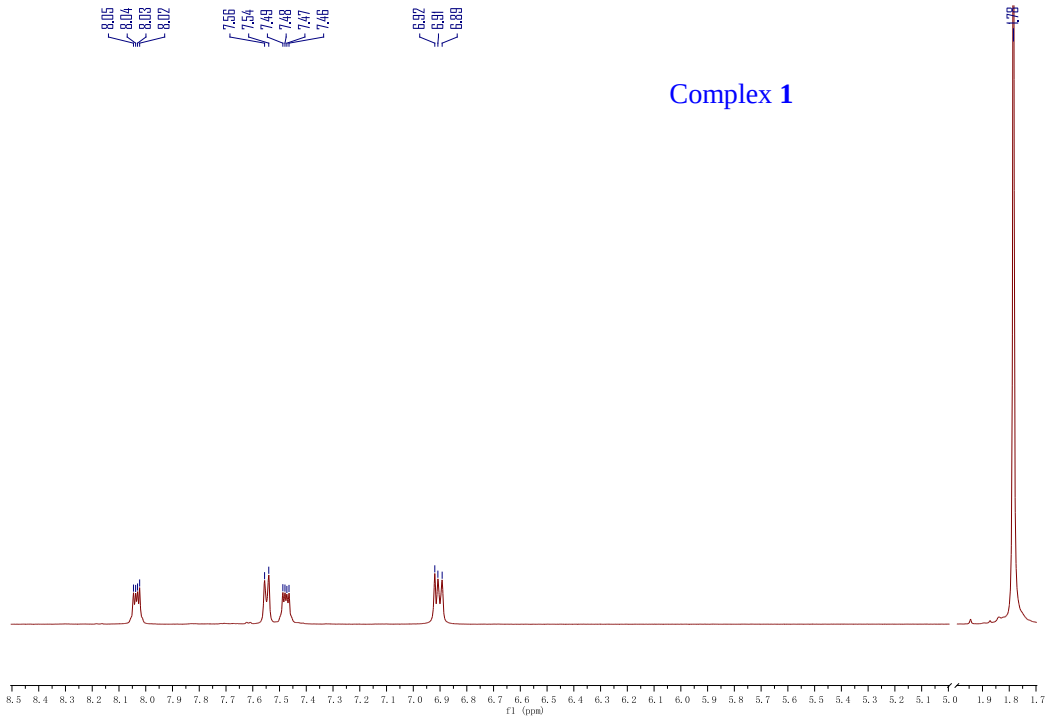


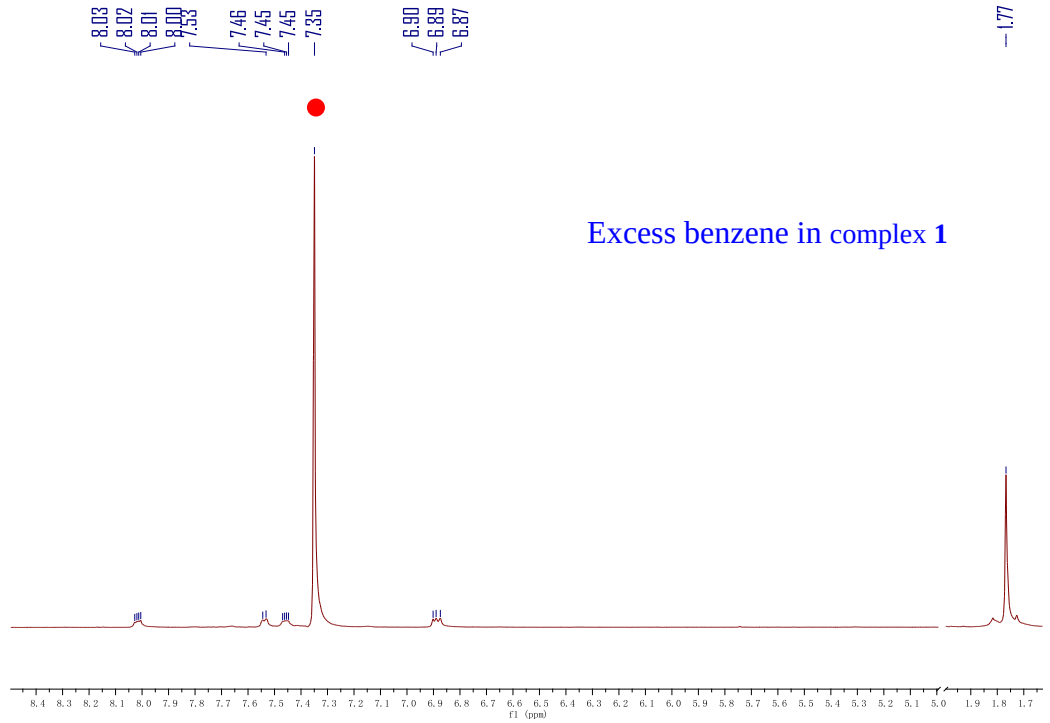
Fig. S5-3 Changes of the chemical shift changes of pyridyl-H (close to the ethenyl) on compelx **1** with addition of Pyrene. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

Naphthalin / Coronene in complex **1**:

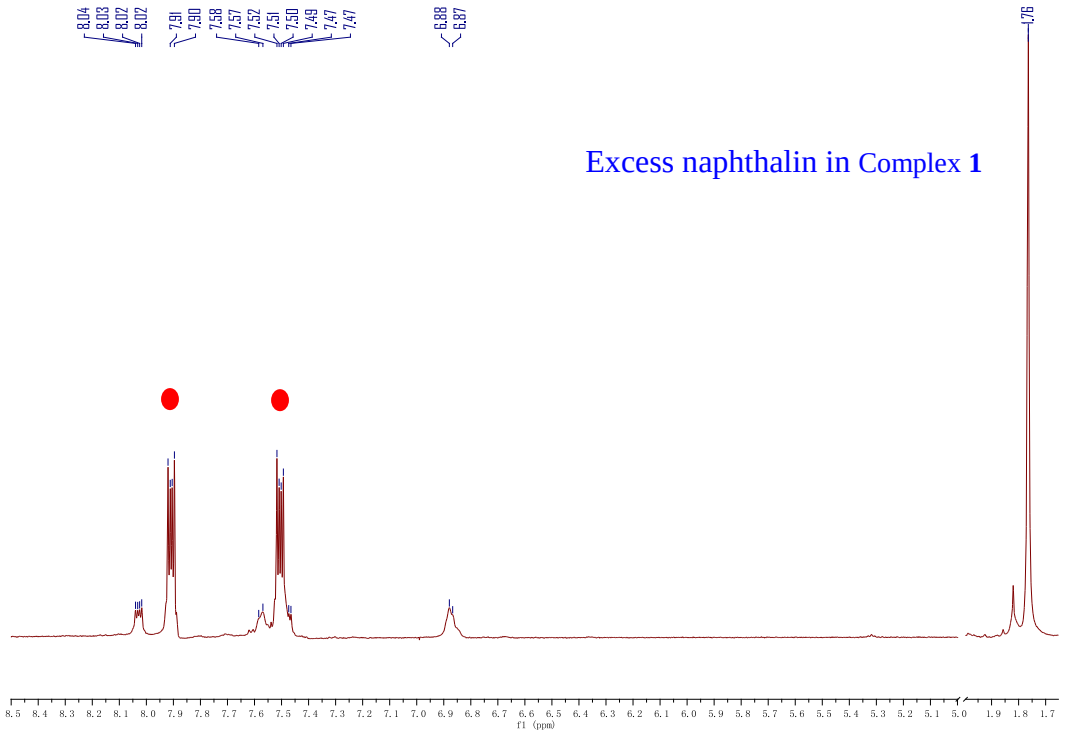
Their max NMR shifts are 0.030 ppm or 0.08 ppm when the guests are excessive(4 equiv/ 2.5 equiv). It's hard to undergo the NMR nitration experiments for K_a. But actually we can get a conclusion that the K_a of naphthalin coronene and other guests were extremely smaller than that of pyrene / pyrene-1-carboxaldehyde.("●" means the signal of guest, all the signal of solvent have been omitted)



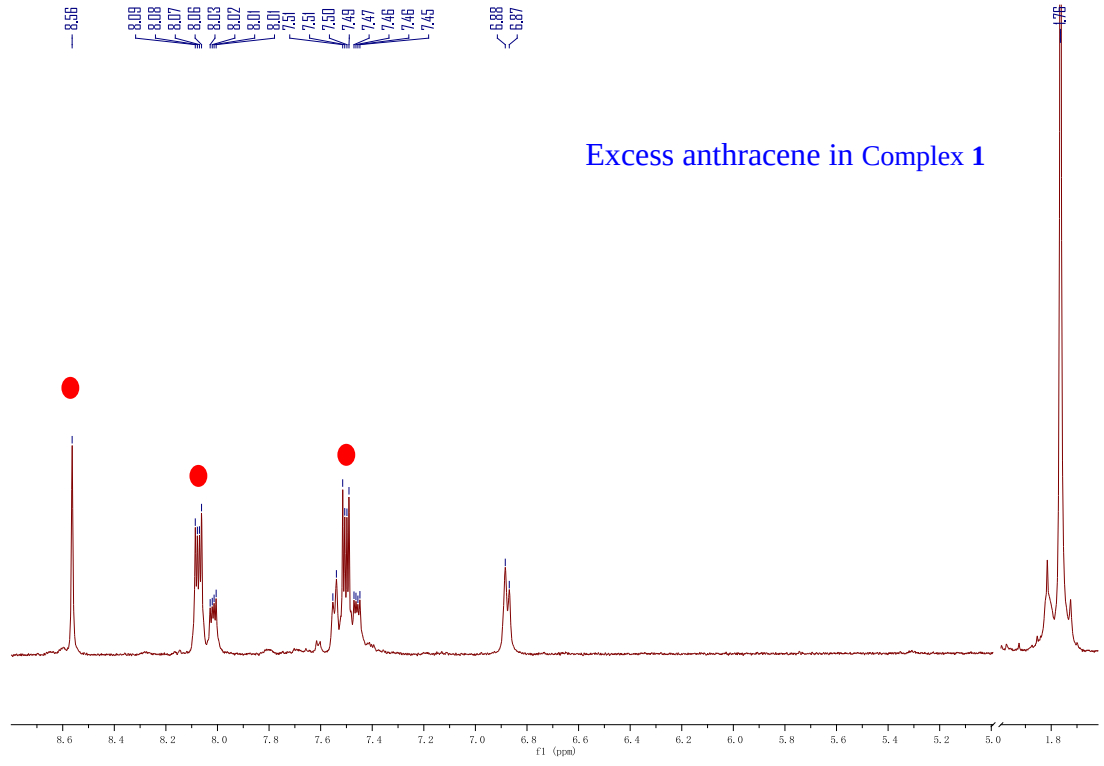
Complex **1**



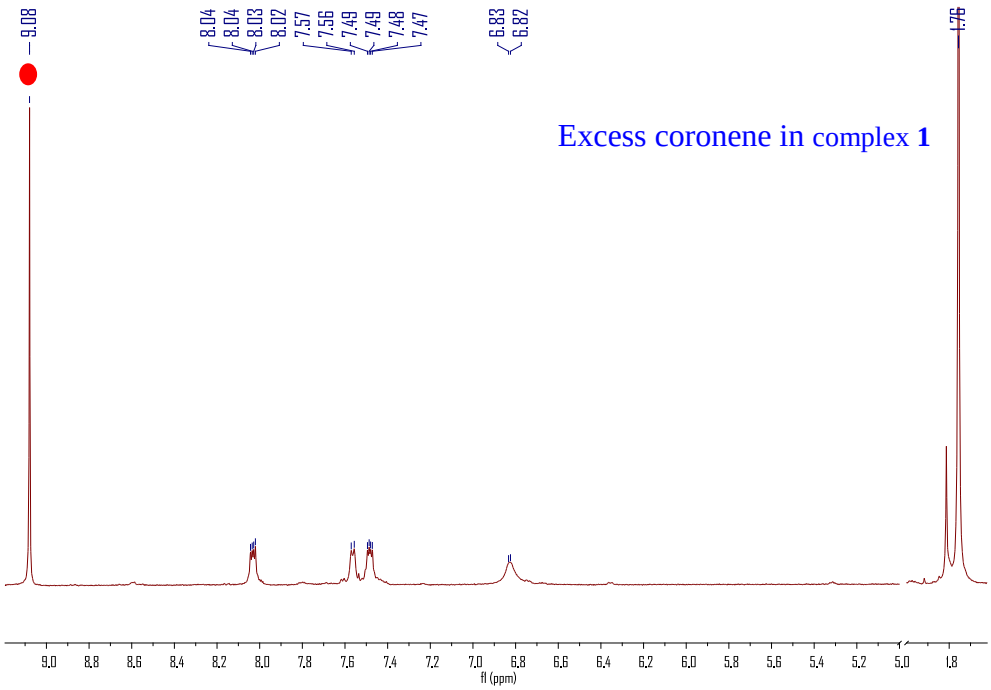
Excess benzene in complex **1**



Excess naphthalin in Complex **1**



Excess anthracene in Complex **1**



[1] Thordarson, P. *Chem. Soc. Rev.* 2011, **40**, 1305-1323.

S6 Inhibition kinetics of the photodimerization

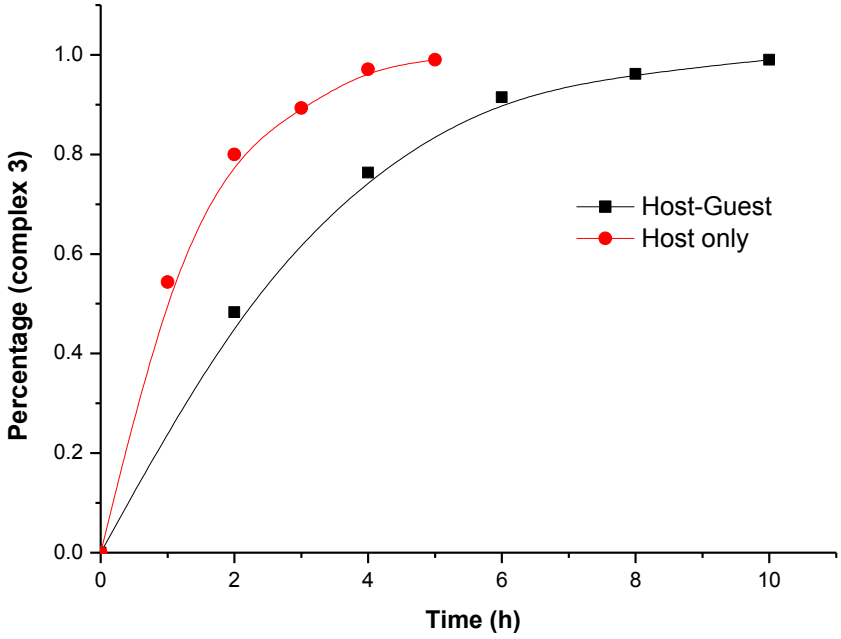


Fig. S6 Percentage of the Cp* NMR signal of complex **3** to all. Red line shows the process from complex **1** to complex **3**; black line shows the process from complex **2** to complex **3**. ([H]=1.0mM, [HG]=1.0mM)

As show in Figure S3, the complex with guest molecule in macrocycle cavity occurred [2+2] *cyclo*-addition a little slowly than empty macrocycle. So that mean the guest molecule play a role as photodimerization-inhibitor.

Synthesis and Characterization:

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System and collected just before use. $[Cp^*IrCl_2]_2$ [12a] and 2,2'-bisbenzimidazole [12b] were prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, Elemental analyses were carried out by Elementar III Vario EI Analyzer. ^{1}H-NMR spectra were obtained on Bruker DMX-500 or Bruker DMX-400 spectrometer in $[D_6]$-DMSO solution.

Synthesis of **1**, **2, 3** and **4**: To a solution of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (40.0 mg, 0.05 mmol) in dry CH_3OH (10 mL) was added 4,4′-bpe (4.6 mg, 0.05 mmol) at room temperature. After vigorous stirring for 3 hours, AgOTf (51.2 mg, 0.20 mmol) was added to the solution and the reaction was carried out. Finally, 2,2'-bisbenzimidazole (11.7 mg, 0.05 mmol) was added into the solution, and vigorous stirring for 5 hours. After the reaction was complete, the solution was filtered to remove undissolved compounds. The pure products were obtained by the recrystallization through the diffusion of ether into the filtrate, giving the crystals of **1** (light yellow, 28.50 mg, 64%). **2** was obtained after adding pyrene-1-carboxaldehyde(1 equiv)/ pyrene(2 equiv) and stirring over 10 minutes, and the bright yellow crystals for **2**(77%, 26.94 mg)/ **4**(68%, 23.80mg). the bright orange crystals of **3** were obtained through SCSC from **1** after one month exposing to the sunlight, or after 16 hours under ultraviolet. Putting the methanol solution of **2** under the ultraviolet for 24 hours also got the complex **3**.

Data of complex **1**: IR (KBr disk): ν = 1617.5 (m, Ar), 1354.1 (m, C=N). ^{1}H-NMR (500 MHz, $[D_4]$-CD_3OD, TMS): δ = 8.02 (dd, 8H, Ar-H), 7.54 (d, 8H, Py-H), 7.46 (dd, 8H, Ar-H), 6.90 (d, 8H, Py-H), 6.88 (s, 4H, olefin-H), 1.77 (s, 60H; Cp*) ppm. Elemental analysis (%) calcd. for $C_{102}H_{120}F_{12}N_{12}O_{18}Rh_4S_4$: C 47.67, H 4.71, N 6.54; Found (%): C 47.33, H 4.87, N 6.51.

Data of complex **2**: IR (KBr disk): ν = 1614.4 (m, Ar), 1682.6 (s, C=O)1350.8 (m, C=N). ^{1}H-NMR (500 MHz, $[D_6]$-CD_3OD, TMS): δ = 10.47(s, 1H, H-C=O)， 8.12

(dd, 8H, Ar-H), 7.96 (d, 8H, Py-H), 7.57 (dd, 8H, Ar-H), 6.44 (d, 8H, Py-H), 5.96 (s, 4H, olefin-H), 8.99, 8.21, 8.02, 7.69, 7.43 (9H, pyrene-H), 1.70 (s, 60H; Cp*) ppm. Elemental analysis (%) calcd. for $C_{117}H_{126}F_{12}N_{12}O_{19}Rh_4S_4$: C 50.69, H 4.58, N 6.06; Found (%): C 50.48, H 4.62, N 6.15.

Data of complex **3**: IR (KBr disk): ν = 1615.1 (m, Ar), 1349.7 (m, C=N). ^{1}H-NMR (500 MHz, [D_6]-CD_3OD, TMS): δ = 8.03 (dd, 8H, Ar-H), 7.54 (d, 4H, Py-H), 7.49 (d, 4H, Py-H), 7.44 (dd, 8H, Ar-H), 6.77 (d, 4H, Py-H), 6.37 (d, 4H, Py-H), 4.32 (s, 4H, cyclobutane), 1.83 (s, 60H; Cp*) ppm. Elemental analysis (%) calcd. for $C_{104}H_{116}F_{12}N_{12}O_{14}Rh_4S_4$: C 49.45, H 4.63, N 6.65; Found (%): C 49.44, H 4.78, N 6.59.

Data of complex **4**: IR (KBr disk): ν = 1614.6 (m, Ar), 1350.8 (m, C=N). ^{1}H-NMR (500 MHz, [D_6]-CD_3OD, TMS): δ = 8.15 (dd, 8H, Ar-H), 8.07 (d, 8H, Py-H), 7.62 (dd, 8H, Ar-H), 6.50 (d, 8H, Py-H), 7.38 (s, 8H, pyrene-H), 7.23 (d, 8H, pyrene-H), 5.34 (t, 4H, pyrene-H), 5.82 (s, 4H, olefin-H), 1.79 (s, 60H; Cp*) ppm. Elemental analysis (%) calcd. for $C_{130}H_{124}F_{12}N_{12}O_{14}Rh_4S_4$: C 54.86, H 4.39, N 5.91; Found (%): C 54.91, H 4.44, N 5.78.

All single crystals were immersed in mother solution and sealed in thin-walled glass. Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated MoKα radiation (λ = 0.71073 Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.