# **Electronic Supplementary Information**

# Cavity partition and functionalization of a [2+3] organic molecular cage by inserting polar P=O bonds

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#### 1. General

All chemicals were purchased from commercial corporations and used without further purification unless otherwise noted. NMR spectra spectroscopic measurements were performed on Bruker 400 NMR spectrometer with tetramethylsilane (TMS) as the internal standard at room temperature. Electrospray ionization mass spectra (ESI-MS) were recorded by a ThermoFisher Scientific LCQ Fleet mass spectrometer in a scan range of 100-2000 amu. Infrared spectra (4000-400 cm<sup>-1</sup>) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. Thermal analyses were performed on a Universal V3.9A TA Instruments from room temperature to 600 °C with a heating rate of 10 °C/min under flowing nitrogen. The powder X-ray diffraction patterns (PXRD) measurements were carried on a Philips X'pert MPD Pro X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature.

## 2. Synthesis of tris(4-formylphenyl) phosphate



Scheme S1 Synthesis of tris(4-formylphenyl) phosphate

An anhydrous tetrahydrofuran solution (50 mL) containing *p*-hydroxybenzaldehyde (5.0 g, 40.9 mmol) was sealed in a 100 mL round-bottom flask. To this solution POCl<sub>3</sub> (2.1 g, 13.6 mmol) and Et<sub>3</sub>N were added successively and dropwise. The reaction mixture was stirred for another 2 h at room temperature, and water was injected carefully to dissolve the white precipitate triethylamine hydrochloride. The mixture was extracted with ethyl acetate, and the organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained after concentrating the organic solvent in vacuo. The pure tris(4-formylphenyl) phosphate was obtained as white crystalline solid after column chromatography with a yield of 92 %. Single crystals of tris(4-formylphenyl) phosphate were obtained from its ethyl acetate solution by slow evaporation in air at room temperature for 3 days. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 10.00 (s, 3H), 7.93 (d, *J* = 8.6 Hz, 6H), 7.43 (d, *J* = 8.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 190.37, 154.34, 134.22, 131.87, 120.69.



Fig. S1 <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of tris(4-formylphenyl) phosphate



Fig. S2 <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectrum of tris(4-formylphenyl) phosphate

#### 3. Synthesis of [2+3] phosphate organic cage

Tris(4-formylphenyl) phosphate (49.2 mg, 0.12 mmol) was dissolve in a 50 mL acetonitrile/chloroform mixture (v/v = 5:1) at room temperature, and then (1*R*,2*R*)-(-)-1,2-cyclohexanediamine (20.6 mg, 0.18 mmol) was added. The solution was stirred for 12 h at room temperature, and the mixture was filtered to a beaker. The cage product (49.5 mg) was obtained as colorless crystals by slow evaporation from the filtrate in air at room temperature with a yield of 78 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 8.13-8.09 (m, 6H), 7.55-7.51 (m, 12H), 7.15-7.02 (m, 12H), 3.37-3.35 (m, 6H), 1.90-1.47 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 159.57, 151.70, 134.00, 129.41, 119.99, 74.17, 32.65, 24.45. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = -20.78. ESI-MS (positive mode in acetonitrile): *m/z* calcd. for C<sub>60</sub>H<sub>60</sub>N<sub>6</sub>O<sub>8</sub>P<sub>2</sub> [M+H]<sup>+</sup>: 1055.40, found 1055.75. FT-IR absorptions (KBr pellets): 2931 (w), 2858 (w), 1643 (w), 1601 (w), 1502 (w), 1300 (w), 1188 (s), 1161 (m), 968 (s), 841 (w).



Fig. S3 <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of cage 1



Fig. S4 <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectrum of cage 1



Fig. S5 <sup>32</sup>P NMR (CDCl<sub>3</sub>) spectrum of cage 1



Fig. S6 Positive ESI-MS of cage 1 in acetonitrile



Fig. S7 FT-IR spectrum of cage 1



Fig. S8 FT-IR spectral comparison between tris(4-formylphenyl) phosphate (black) and cage 1 (red)

## 4. X-Ray data collection and structural determination

Single-crystal samples were covered with glue and mounted on glass fibers and then used for data collection. Crystallographic data were collected on a Bruker SMART 1K CCD diffractometer, using graphite mono-chromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected data were reduced by using the program SAINT and empirical absorption corrections were done by SADABS program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. In the case of cage 1, it is found that the solvent molecules were highly disordered. Attempts to locate and refine the solvent peaks were unsuccessful. So contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*. The summary of the crystal data, experimental details and refinement results for tris(4-formylphenyl) phosphate and cage 1 is listed in Table S1.



Fig.S9 Crystal structures of tris(4-formylphenyl) phosphate (A) and cage 1(B)



Fig. S10 A photographic image for single crystals of cage 1



**Fig. S11** Perspective view of the window in cage 1 with a diameter of 4.0 Å (represented by a purple ball) from different directions

Compound	Tris(4-formylphenyl) phosphate	Cage 1	
Empirical formula	C <sub>21</sub> H <sub>15</sub> O <sub>7</sub> P	$C_{60}H_{60}N_6O_8P_2$	
Formula weight	410.30	1055.08	
Temperature	291(2) K	291(2) K	
Wavelength	0.71073 Å	0.71073 Å	
Crystal system	monoclinic	cubic	
Space group	P2 <sub>1</sub> n	<i>P</i> 2 <sub>1</sub> 3	
a	7.7879(13) Å	19.1327(11) Å	
b	20.327(3) Å	19.1327(11) Å	
С	11.9549(19) Å	19.1327(11) Å	
α	90°	90°	
β	93.558(3) °	90°	
γ	90°	90°	
Volume	1888.9(5) Å <sup>3</sup>	7003.7(7) Å <sup>3</sup>	
Ζ	4	4	
Density (calculated)	1.443 mg/m <sup>3</sup>	1.001 mg/m <sup>3</sup>	
Absorption coefficient	0.188 mm <sup>-1</sup>	0.110 mm <sup>-1</sup>	
F(000)	848	2224	
Crystal size	0.12 x 0.12 x 0.10 mm <sup>3</sup>	0.14 x 0.12 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.98 to 26.00°	1.51 to 25.01°	
Index ranges	$-9 \le h \le 9$ , $-25 \le k \le 24$ , $-14 \le l \le 14$	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -22 ≤ l ≤ 20	
Reflections collected	15047	52238	
Independent reflections	3707 [R(int) = 0.0831]	4127 [R(int) = 0.1303]	
Completeness	99.9 %	99.4 %	
Max. and min. transmission	0.9814 and 0.9778	0.9891 and 0.9848	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	
Data / parameters	3707 / 262	4127 / 229	
Goodness-of-fit on F <sup>2</sup>	0.988	1.136	
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0692, wR <sub>2</sub> = 0.1813	$R_1 = 0.0989$ , w $R_2 = 0.2181$	
R indices (all data)	R <sub>1</sub> = 0.0882, wR <sub>2</sub> = 0.1957	$R_1 = 0.1512$ , $wR_2 = 0.2456$	
Largest diff. peak and hole	1.297 and -0.595 e·Å <sup>-3</sup>	0.317 and -0.222 e·Å⁻³	

 Table S1 Crystal data and structure refinement for tris(4-formylphenyl) phosphate and cage 1

# 5. Powder X-ray diffraction



Fig. S13 Powder X-ray diffraction pattern for cage 1

# 6. Thermogravimetric (TGA) data for cage 1



Fig. S14 Thermogravimetric (TGA) data for cage 1

## 7. Gas Sorption Analysis

In the gas sorption measurement, ultra-high-purity grade  $CH_4$  (> 99.999 %) and  $CO_2$  gases (99.995 % purity) were used throughout the adsorption experiments. Sample was degassed at offline at 80 °C for 12 h in vacuo (10<sup>-5</sup> bar) before analysis. Low-pressure  $CH_4$  and  $CO_2$  adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area analyzer. <sup>1</sup>H NMR spectral comparison of cage 1 before and after gas sorption is shown in Fig. S15.



Fig. S15 <sup>1</sup>HNMR spectral comparison of cage 1 before and after gas sorption

Compound	$CO_2$ uptake	$CH_4$ uptake	Ideal selectivity	Reference
[4.4]				C1
[4+4]	4.1 <sup>(0)</sup>	1.3 [0]	3.2	51
[4+6]- <i>t</i> Bu	2.7 <sup>[a]</sup>	0.7 <sup>[a]</sup>	3.9	S2
[4+6]-exo	3.4 <sup>[a]</sup>	0.7 <sup>[a]</sup>	4.9	S3
[2+3] cage	2.7 <sup>[b]</sup>	0.7 <sup>[b]</sup>	3.9	S4
[2+3]-extend	3.3 <sup>[b]</sup>	0.3 <sup>[b]</sup>	11	S4
CC1α'	1.27 <sup>[c]</sup>	0.55 <sup>[c]</sup>	2.3	S5
CC2	3.0 <sup>[c]</sup>	1.13 <sup>[c]</sup>	2.7	S5
CC3	2.47 <sup>[c]</sup>	1.53 <sup>[c]</sup>	1.6	S5
CC6	0.9 <sup>[d]</sup>	n.d.		S6
ZCs	0.1-0.25 <sup>[e]</sup>	n.d.		S7
[4+6]- triazine	38.6 <sup>[f]</sup>	16.4 <sup>[f]</sup>	2.4	S8
PB-2			47.9 <sup>[g]</sup>	S9

Table S2 Summary of CO<sub>2</sub> uptake, CH<sub>4</sub> uptake and ideal selectivity (CO<sub>2</sub>/CH<sub>4</sub>) in selected porous materials

[a] Measured at 273 K, 1 bar; [b] at 298 K, 1 bar; [c] at 275 K, 1 bar; [d] at 300 K, 1.2 bar; [e] at 293 K, 1 bar; [f] cm<sup>3</sup>g<sup>-1</sup>, at 273 K, 1.08 bar; [g] IAST selectivity, at 273 K, 1 bar.

## 8. Calculation Details

To further analyze the binding energies between two cages (Fig. S16) and  $CO_2/CH_4$  molecules at different adsorption sites, density functional theory with the B3LYP hybrid exchange correlation functional<sup>S10</sup> was used in this study. The split-valance basis set 6-31+G(d)<sup>S11</sup> with polarization and diffuse functions on all atoms were employed and the Berny algorithm<sup>S12</sup> based on energy minimization was used for geometry optimization. The optimized geometry structure of the cage 1 is shown in Fig. S16A. In order to clarify the effect of P=O bonds to cage 1, a similar cage as cage 1 without P=O bonds is built and optimized using the same method (Fig. S16B). IR spectra were calculated to ensure that all reported conformations have only real and positive frequencies. The Gaussian 09 package<sup>S13</sup> was used throughout. The binding energy is defined as  $E_{Binding}=E_{cav+mol}-E_{cav}-E_{mol}$ , where  $E_{Binding}$  is the binding energy,  $E_{cav+mol}$  is the energy of gas molecule captured cavity,  $E_{cav}$  and  $E_{mol}$  are the energies of the cavity and the gas molecule, respectively.



Fig. S16 Optimized structures with and without the P=O bonds



E<sub>binding</sub> = -4.8 KJ mol<sup>-1</sup>

Fig. S17 Optimized cage complex in the absence two P=O bonds with CO<sub>2</sub> adsorbed around the imine site



Ebinding= -8.84 KJ mol<sup>-1</sup>

Fig. S18 Optimized cage 1 complex with CO<sub>2</sub> adsorbed around other three outer-directed P–O bonds

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