Electronic Supplementary Information (ESI)

Pillar[5]arene-containing cross-linked polymer: synthesis, characterization, and adsorption of dihaloalkanes and n-alkylene dinitriles

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1. *Materials and methods*

All reagents were purchased from commercial sources and used without further purification, unless otherwise noted. Commercially available Merrifield resin **CMPS** (1% DVB cross linked, 100~200 mesh, 2.4 mmol equivalent of Cl/g of resin) was purchased from Aladdin. Monohydroxy pillar[5]arene **HOP5** was prepared according to the literature procedure(S1). GC analyses were obtained on a Thermo Scientific Focus GC Gas Chromatograph equipped with a DB-5 30 m × 0.25 mm ID × 0.25 μm capillary column (Agilent) and an FID detector. The following GC oven temperature programs were used: 90 °C hold for 2 min, ramp 10 °C/min to a final temperature of 280 °C, and hold for 3 min. Nitrogen was used as a carrier gas, with a constant column flow of 2.0 mL/min. The injector temperature was held at 260 °C. FT-IR spectra were performed on a VERTEX 70 spectrometer. Solid-13C NMR spectra were obtained on an Avance III HD 400 spectrometer. TGA were performed on a STA449 F3 simultaneous Thermal Analyzer. Elemental analysis were performed on Vario EL Cube, Elementar.

2. *Synthesis of polymeric pillar[5]arene (PS-P5)*

CMPS (830 mg, 2 mmol) and **HOP5** (1000 mg, 1.36 mmol) were mixed in the acetone solution. Then K_2CO_3 (2.2 g, 1.6 mmol) and KI (600 mg, 3.6 mmol) were added to the suspension. The mixture was stirred under reflux for 5 days under argon atmosphere. The solid was filtered and washed with water and acetone to give **PS-P5**

as white powder. From the filtrate, 242 mg of unreacted **HOP5** was recycled. The amount of loaded pillar[5]arene on the polymeric support was evaluated by the difference of mass taken before and after the coupling reaction of **HOP5**. The result showed that 50% of the chlorine content was converted to pillar[5]arene moieties, which was calculated to be 50 mol % functionalization, leading to the acquirement of 1.2 mmol chlorine and 1.2 mmol pillar[5]arene units per gram of **PS-P5**.

3. Standard curves of the eight adsorbates

The typical process for the standard curves of eight adsorbates: we firstly prepared a series of DBB solutions with different concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450, 500 μg/mL) in toluene, then measured the corresponding peak areas by Gas Chromatography. Finally, the relationship between the peak areas and the concentrations were obtained using Origin software. The results showed that the peak areas had good linear relations with the concentrations of all the eight adsorbates.

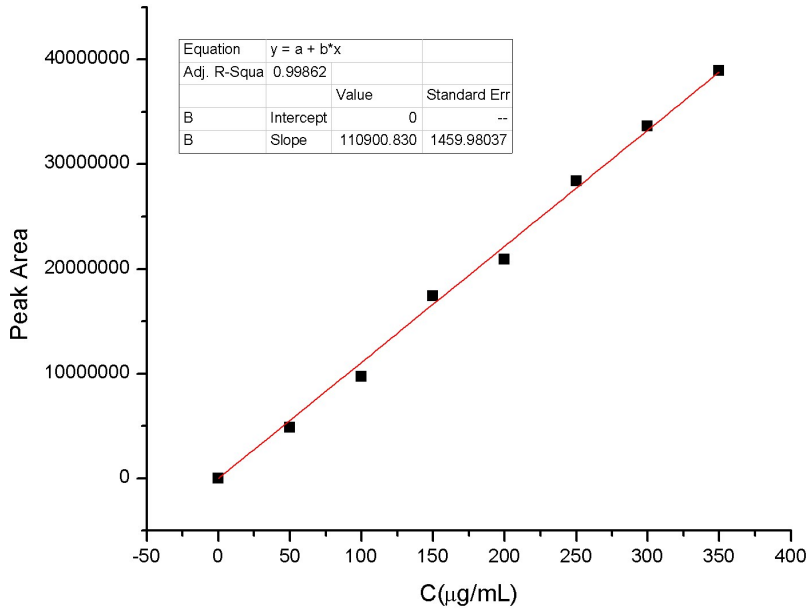

Fig. S1. Standard curve of **DCB**.

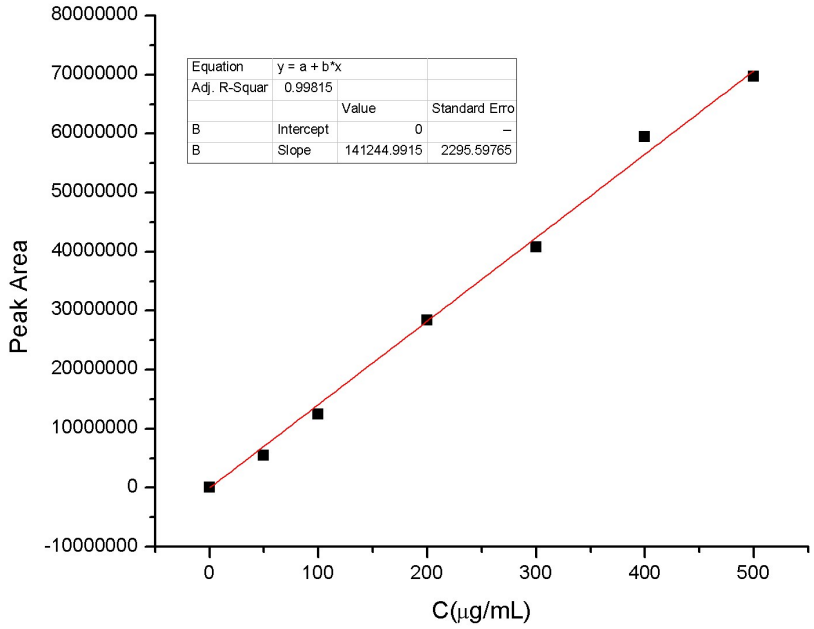

Fig. S2. Standard curve of **DCH**.

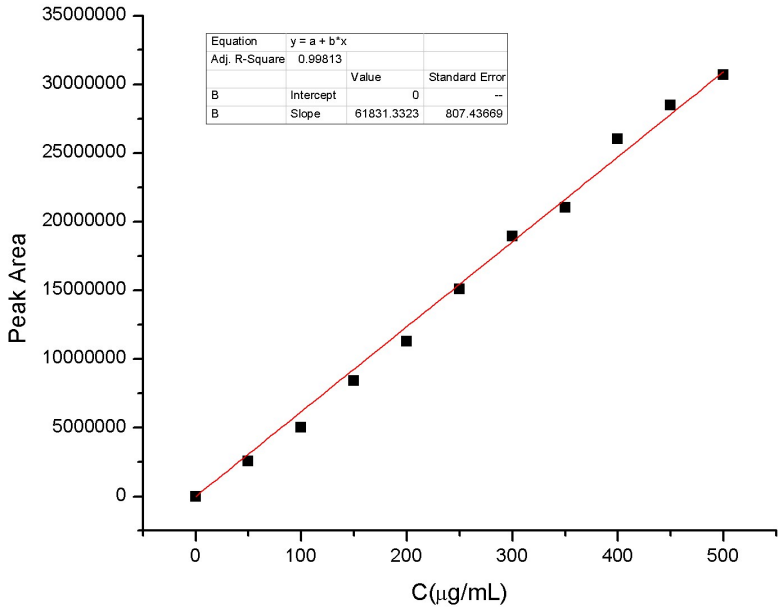

Fig. S3. Standard curve of **DBB**.

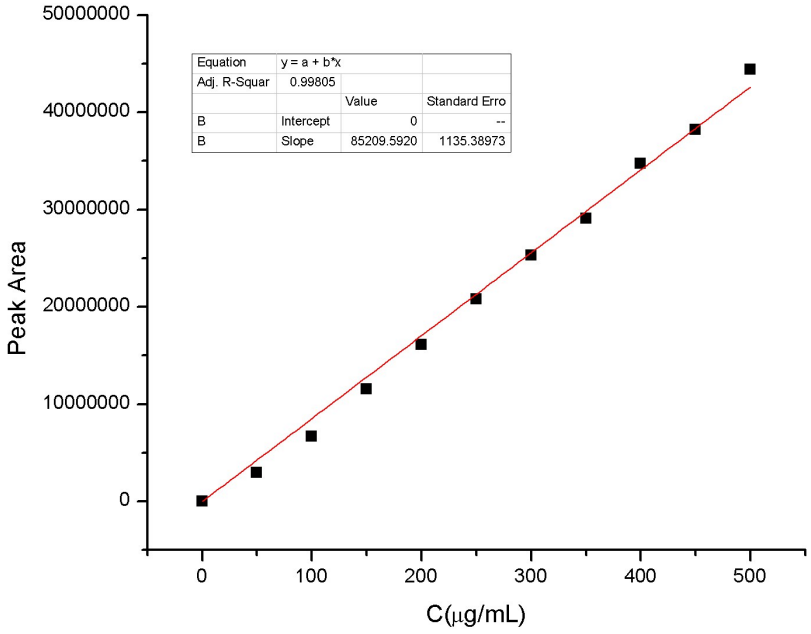

Fig. S4. Standard curve of **DBH**.

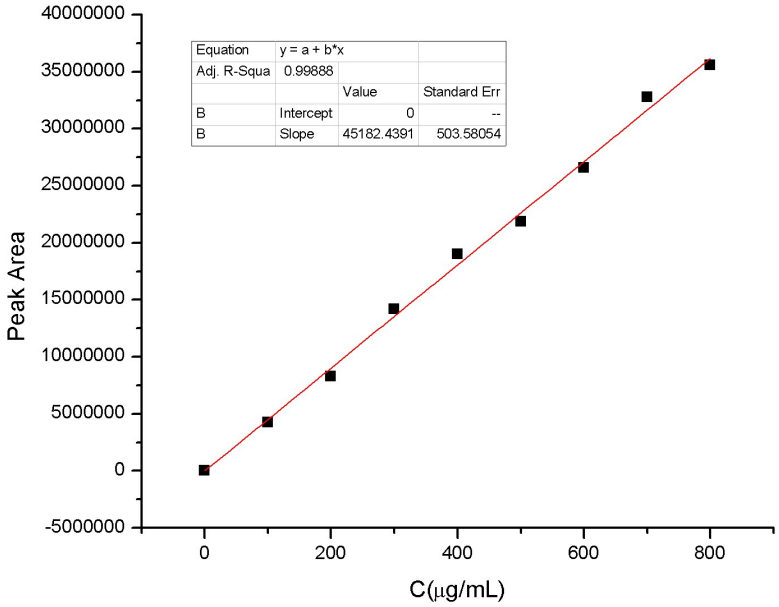

Fig. S5. Standard curve of **DIB**.

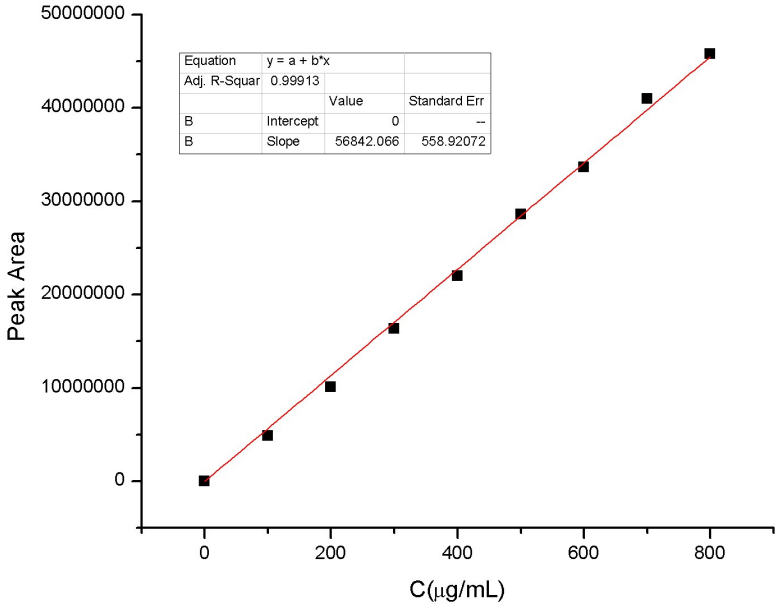

Fig. S6. Standard curve of **DIH**

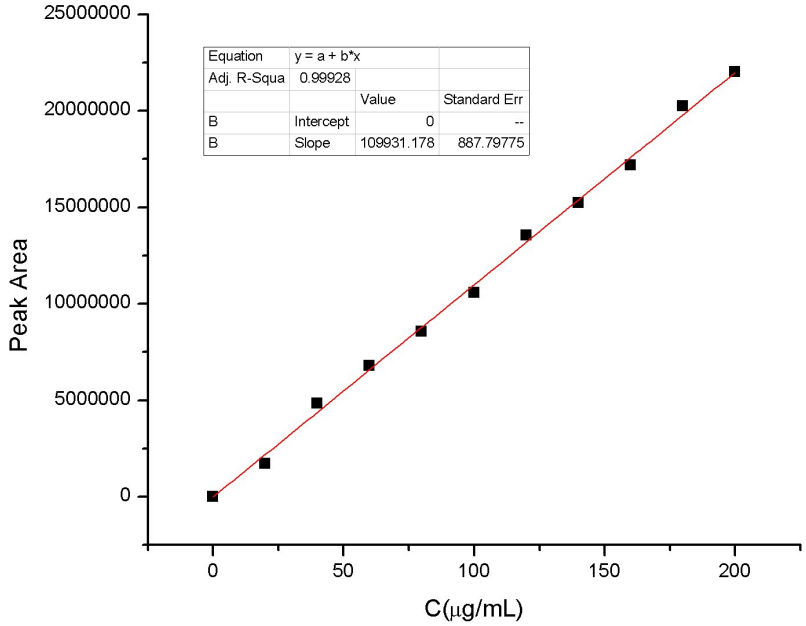

Fig. S7. Standard curve of **DNB**.

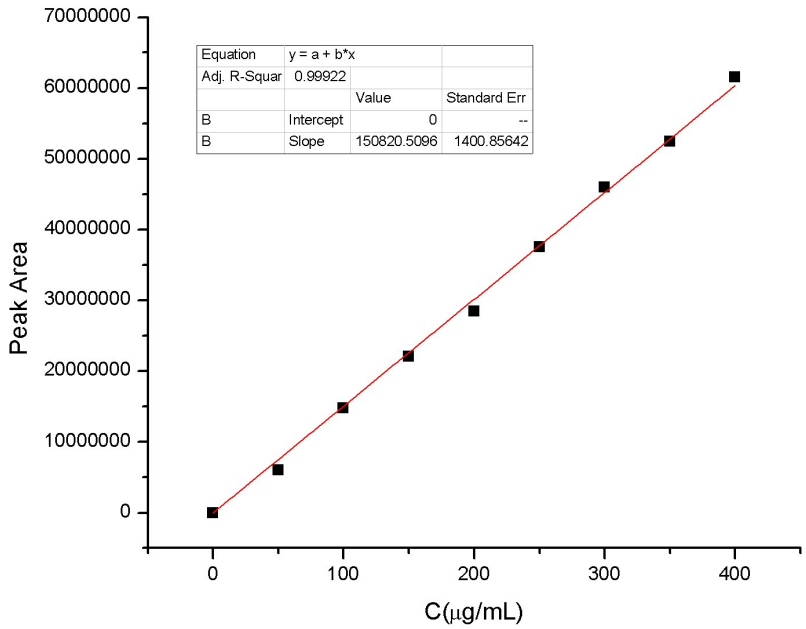

Fig. S8. Standard curve of **DNH**.

4. Thermogravimetric analysis of PS-P5 and CMPS

The first step (250~300 ℃) of weight loss of **PS-P5** (curve b) can primarily be ascribed to the loss of water and solvent desorption from the solid materials, followed by a plateau until 400 ℃. Then the second weight loss step (400~500 ℃) is ascribed to the pillar[5]arene and **CMPS** decomposition. The residual weight percentage for **HOP5** is about 45% when heated to 800 ℃ (curve a) , while it is about 15% for **CMPS** (curve c). For **PS-P5**, the corresponding residual weight is about 30% , indicating that pillar[5]arene **HOP5** was successfully modified on **CMPS**.

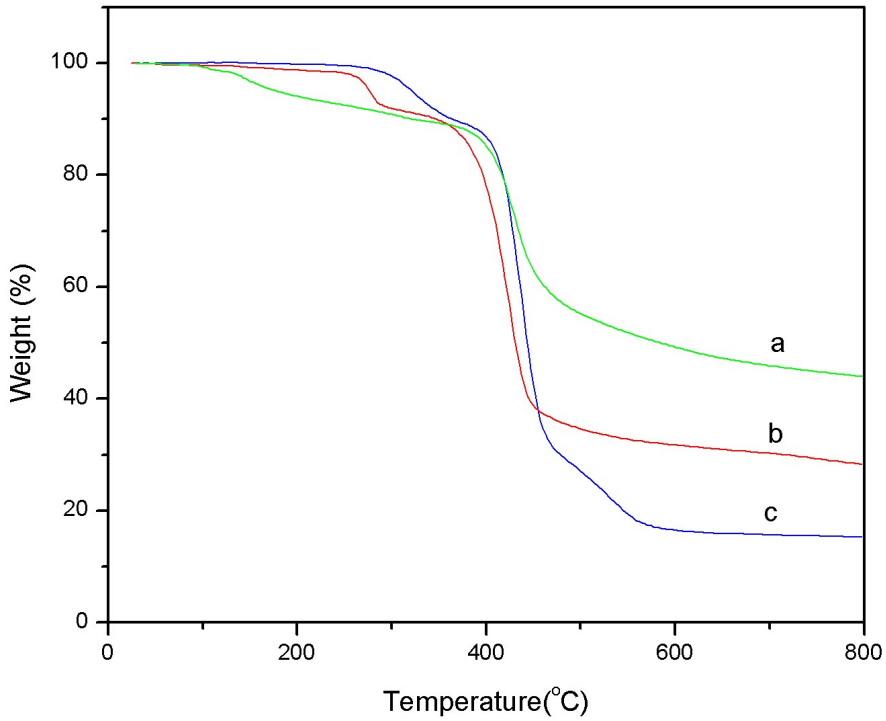

Fig. S9. TGA curves of (a) **HOP5**, (b) **PS-P5**, (c) **CMPS**

5. Elemental analysis of HOP5, PS-P5 and CMPS

Table S1. The element contents of **HOP5, PS-P5** and **CMPS**.

Samples	Element content (Average)	
	C[%]	H[%]
HOP5	70.97	6.462
PS-P5	79.49	6.843
CMPS	85.72	7.002

6. Exponential function between the adsorbed amount of DBB and time

The adsorbed amount of DBB on column and time meet exponential function as below: $y = 3995.5 - 3476.4 * exp\ (-0.02\ x)$

	A	B	C	D
1	Equation	y = y0 + A*exp(R0*x)		
2	Adj. R-Square	0.99337		
3			Value	Standard Error
4	B	y0	3995.46558	104.01435
5	B	A	-3476.41397	86.71847
6	B	R0	-0.02022	0.00184

Fig.S10 Exponential function between the adsorbed amount of DBB and time

Moreover, the differential equation of the exponential function is calculated as below:

$y^{'} = 69.528 * exp\ (-0.02\ x)$

As is depicted in the differential equation, the adsorption rate of the **PS-P5** column toward DBB decreases gradually over time and reached equilibrium eventually.

7. Association constants Ka of the host-guest inclusion complexation

Table S2. Association constants Ka of the host-guest inclusion complexation.

Host	Guest	K_a (M^{-1})
EtP5A[a]	DCB	（1.9±0.2）× 10^3
EtP5A[a]	DBB	（4.9±0.3）× 10^3
EtP5A[a]	DIB	（1.0±0.1）× 10^4
EtP5A[b]	DNB	--[c]
EtP5A[b]	DNH	（1.5±0.3）× 10^4

[a] In $CDCl_3$, 298 K.

[b] In the mixture of DMSO-d_6 : $CDCl_3$ (1:9, v:v), 298K.

[c] The free guest DNB is not observed in the presence of one equivalent of EtP5A host, suggesting very strong binding affinities in 1:9 DMSO-d_6:$CDCl_3$. The value is (3.6 ± 0.2) × 10^3 M^{-1} in DMSO-d_6:$CDCl_3$ (5 : 5).

7. Reversibility of PS-P5

The reversibility of **PS-P5** was tested. The initial adsorption ratio of fresh **PS-P5** toward DBB is 56.1%. Then acetone was added to **PS-P5** and the mixture was stirred for 12 h. The solid was filtered and washed with acetone. The recovered **PS-P5** was dried and used to the next adsorption experiment. The process above was repeated for three times and the results were shown in Table S3.

Table S3. The reversibility of **PS-P5**.

Cycles	Adsorption Ratio (%)
Cycle 1	56.1
Cycle 2	55.8
Cycle 3	54.9
Cycle 4	54.7

When PS-P5 was regenerated and reused for three recycles, the adsorption ratio can still reach to 97.5% of the initial 56.1%.

References:

S1. (a) T. Ogoshi, K. Demachi, K. Kitajima and T. A. Yamagishi, Chem. Commun., 2011, **47**, 7164-7166; (b).Y. Chen, M. He, B. Li, L. Wang, H. Meier and D. Cao, RSC Adv, 2013, **3**, 21405-21408.