

## Supporting Information

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Incorporating Two Crown Ether Struts into the Backbone of Robust Zirconium-Based Metal–Organic Frameworks as Custom-Designed Efficient Collectors for Radioactive Metal Ions

*Lei Li, Kang Kang, Tien-Shee Chee, Zhenjiang Tian, Qi Sun and Chengliang Xiao\**

## Supporting Information

### **Incorporating Two Crown Ether Struts into the Backbone of Robust Zirconium-based Metal-Organic Frameworks as Custom-Designed Efficient Collectors for Radioactive Metal Ions**

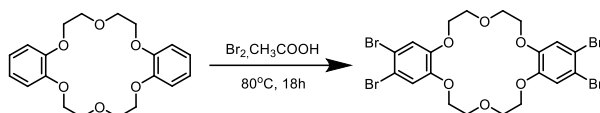
*Lei Li, Kang Kang, Tien-Shee Chee, Zhenjiang Tian, Qi Sun, and Chengliang Xiao\**

#### **Materials and instrumentation**

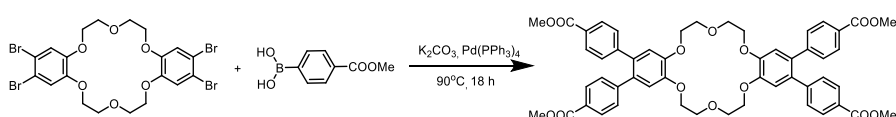
All starting materials were purchased from commercial companies and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Ultima IV diffractometer equipped with Cu K $\alpha$  radiation from 3° to 60° with a step of 0.02°. The porous properties of the samples were measured by N<sub>2</sub> physisorption at 77 K on an automated specific surface area and micropore analyzer (AUTOSORB-IQ2-MP). TG analysis was performed in a nitrogen atmosphere with a rate of 10 °C min<sup>-1</sup> using a TA Instruments SDT Q600. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Thermo Scientific ESCALAB 250Xi. FT-IR spectra were obtained on a Nicolet 6700 spectrometer in KBr pellets in the wavelength range of 4000 – 400 cm<sup>-1</sup>. EDS images were acquired on a Scanning Electron Microscopy with an Energy Dispersive X-ray Spectrometer (SEM-EDS, Hitachi SU8010). The concentrations of Sr<sup>2+</sup> and Cs<sup>+</sup> in solutions were analyzed by an ICP-MS (Agilent Technologies 7800). The Single-crystal X-ray diffraction data collection of ZJU-X100, Sr<sup>2+</sup>⊂ZJU-X100 and Cs<sup>+</sup>⊂ZJU-X102 were recorded on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Cu-K $\alpha$  radiation). The Single-crystal X-ray diffraction data collection of ZJU-X102 was recorded on a Bruker D8-Venture diffractometer with an X-ray Source (Ga-K $\alpha$  radiation). The data frames were collected using the program APEX 3 and processed using the program SAINT routine in APEX 3. The crystal structures were refined by the full-matrix least-squares on  $F^2$  using the SHELXTL-2018 program.

#### **Experimental section**

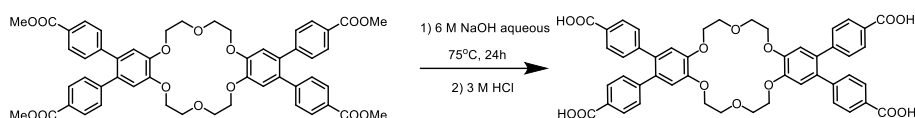
##### **Synthesis of Linkers.**



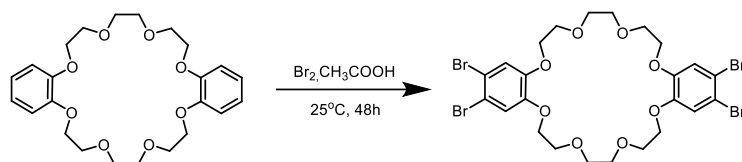
**4,4',5,5'-tetrabromodibenzo-18-crown-6.** Dibenzo 18-crown-6 (12.50 g, 27.7 mmol) was dissolved in acetic acid (230 ml). Bromine (13.30 ml, 260.4 mmol) was added to the solution, and the mixture was stirred for 18 h at 80 °C. After cooling the solution, the orange powder was filtered and washed with MeOH and water to give white residue (19.25 g, 82.12%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.03 (s, 4 H), 4.10 (t, 8 H), 3.96 (t, 8 H).



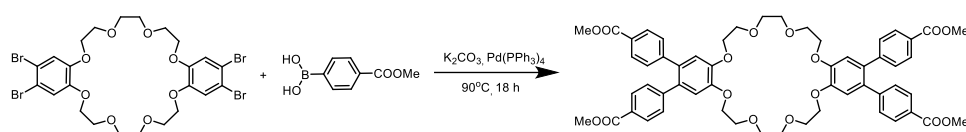
**4,4',5,5'-tetrabenzoate dibenzo-18-crown-6.** 4,4',5,5'-tetrabromodibenzo-18-crown-6 (11.30 g, 16.71 mmol), 4-methoxycarbonylphenylboronic acid (18.06 g, 100.35 mmol), K<sub>2</sub>CO<sub>3</sub> (23.1 g, 167.3 mmol), and tetrakis(triphenylphosphine) palladium (1.35 g, 1.17 mmol) were added into a 1 L Schleck flask. The flask was pumped under vacuum and refilled with Ar gas three times, and then the degassed solvent of 1,4-dioxane/CH<sub>3</sub>OH (540 mL/180 mL) were transferred into the Schleck flask. The mixture solution was heated at 90 °C for 18 h under an Ar atmosphere. After that the reaction mixture was cooled to room temperature. It was concentrated by a rotary evaporator and washed by saturated NaCl solution. Finally, the crude product was recrystallized with ethyl acetate and CH<sub>2</sub>Cl<sub>2</sub> to obtain a white solid. Yield: 9.18 g (61.24 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.87 (d, 8 H), 7.14 (d, 8 H), 6.94 (s, 4 H), 4.26 (t, 8 H), 4.08 (t, 8 H), 3.89 (s, 12 H).



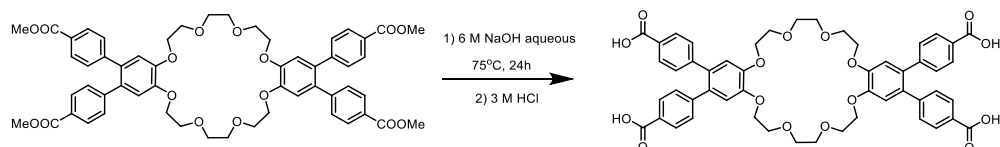
**4,4',5,5'-terabenzoic acid dibenzo-18-crown-6.** 4,4',5,5'-tetrabenzoate dibenzo-18-crown-6 (14.7 g, 0.966 mmol) was dissolved in 550 mL of CH<sub>3</sub>OH, and 183 mL of 6 M NaOH aqueous solution was added. The mixture was stirred under 75 °C for 24 h. After cooling to room temperature, it was concentrated under vacuo to remove methanol. 3 M HCl was added to the above solution and adjusted to pH = 1. white precipitate was obtained by centrifugation and washed with water and dried in vacuum oven at 70 °C for 12 h. Yield: 11.58 g (84.03%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  = 7.78 (d, 8 H), 7.22 (d, 8 H), 7.03 (s, 4 H), 4.22 (t, 8 H), 3.88 (t, 8 H).



**4,4',5,5'-tetrabromodibenzo-24-crown-8.** Dibenzo 24-crown-8 (9.00 g, 20.07 mmol) was dissolved in acetic acid (120 ml). Bromine (8.1 ml, 153.78 mmol) was added to the solution, and the mixture was stirred for 48 h at 25 °C. After cooling the solution, the orange powder was filtered and washed with MeOH and water to give a white residue (10.68 g, 69.6 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.06 (s, 4 H), 4.10 (t, 8 H), 3.89 (t, 8 H), 3.79 (s, 8 H).



**4,4',5,5'-tetrabenzoate dibenzo-24-crown-8.** 4,4',5,5'-tetrabromodibenzo-24-crown-8 (11.00 g, 14.44 mmol), 4-methoxycarbonylphenylboronic acid (15.46 g, 85.9 mmol), K<sub>2</sub>CO<sub>3</sub> (19.79 g, 143.14 mmol), and tetrakis(triphenylphosphine) palladium (1.15 g, 0.99 mmol) were added into a 1 L Schleck flask. The flask was pumped under vacuum and refilled with Ar gas three times, and then the degassed solvent of 1,4-dioxane/CH<sub>3</sub>OH (540 mL/180 mL) were transferred into the Schleck flask. The mixture solution was heated at 90 °C for 18 h under an Ar atmosphere. After that the reaction mixture was cooled to room temperature. It was concentrated by a rotary evaporator and washed by saturated NaCl solution. Finally, the crude product was recrystallized with ethyl acetate and CH<sub>2</sub>Cl<sub>2</sub> to obtain a white solid. Yield: 8.62 g (60.78 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.86(d,8 H), 7.14 (d, 8 H), 6.94 (s, 4 H), 4.24 (t, 8 H), 3.97 (t, 8 H), 3.89 (s, 12 H).



**4,4',5,5'-terabenzoic acid dibenzo-24-crown-8.** 4,4',5,5'-tetrabenzoate dibenzo-24-crown-8 (13.4 g, 0.966 mmol) was dissolved in 460 mL of CH<sub>3</sub>OH, and 153 mL of 6 M NaOH aqueous solution was added. The mixture was stirred under 75 °C for 24 h. After cooling to room temperature, it was concentrated under vacuo to remove methanol. 3 M HCl was added to the above solution and adjusted to pH=1. White precipitate was obtained by centrifugation and washed with water and dried in vacuum oven at 70 °C for 12 h. Yield: 10.68 g (84.56 %). <sup>1</sup>H

NMR (500 MHz, DMSO- $d_6$ , 298 K):  $\delta$  = 7.78 (d, 8 H), 7.21 (d, 8 H), 7.04 (s, 4 H), 4.21 (t, 8 H), 3.81 (t, 8 H), 3.71 (s, 8 H).

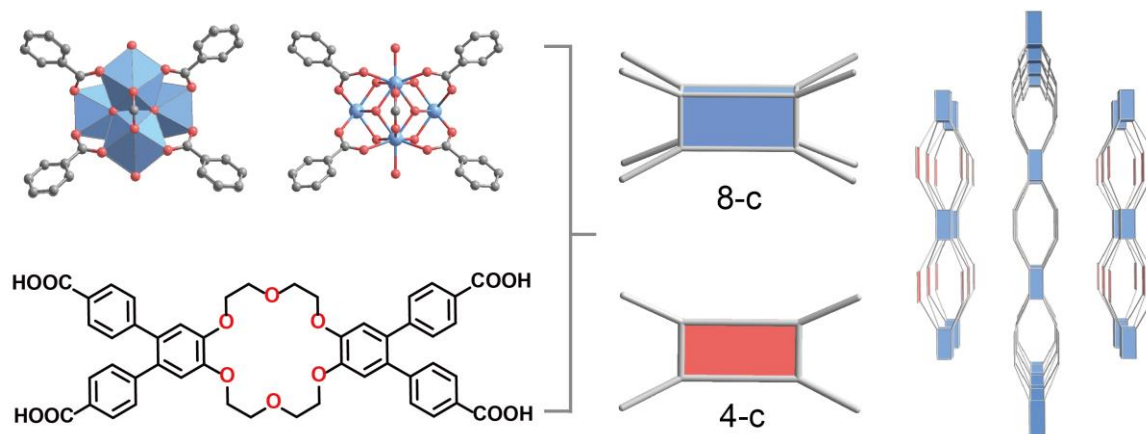
**Synthesis of ZJU-X100.** The ligand of L1(4,4',5,5'-terabenzic acid dibenzo-18-crown-6) (10 mg, 0.0119 mmol) and  $ZrOCl_2 \cdot 8H_2O$  (11.5 mg, 0.0356 mmol) were added in 6 mL of DMF/formic acid (v/v, 4/2) solution. The mixture was placed into a Teflon-lined stainless-steel autoclave and heated at 120 °C for 48 h. After cooling to room temperature, the crystals were isolated by filtration, then washed with DMF, EtOH and dried at 50 °C for 12 h (Yield: 53% based on L1). The crystal data of ZJU-X100 is presented in **Table S2**.

**Synthesis of ZJU-X102.** The ligand of L2(4,4',5,5'-terabenzic acid dibenzo-24-crown-8) (45 mg, 0.0484 mmol),  $ZrOCl_2 \cdot 8H_2O$  (17.5 mg, 0.0543 mmol) and 80  $\mu$ L TFA were added in 6 mL of DMF/formic acid (v/v, 4/2) solution. The mixture was placed into a Teflon-lined stainless-steel autoclave and heated at 120 °C for 72 h. After cooling to room temperature, the crystals were isolated by filtration, then washed with DMF, EtOH and dried at 50 °C for 12 h (Yield: 62% based on L2). The crystal data of ZJU-X102 is presented in **Table S3**.

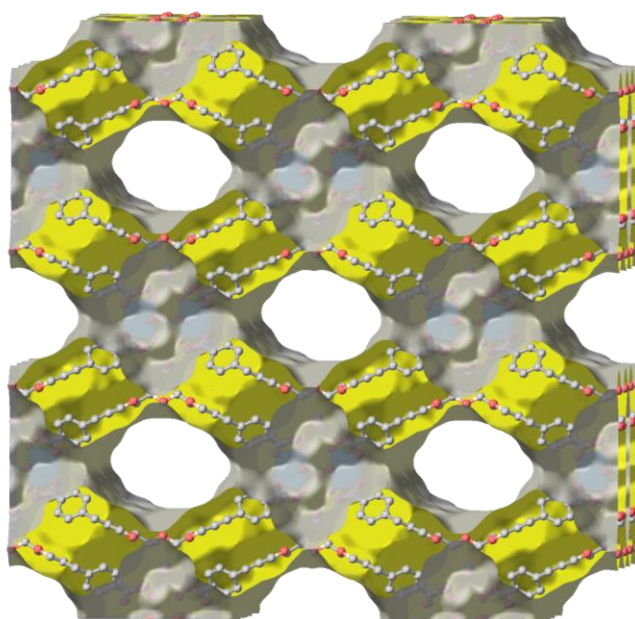
**Synthesis of  $Sr^{2+} \subset ZJU-X100$ .** The synthesized ZJU-X100 was immersed in the  $SrCl_2$  saturated solution. The solution was replenished more than 5 times for 1 day. The crystal data of  $Sr^{2+} \subset ZJU-X100$  is presented in **Table S4**.

**Synthesis of  $Cs^+ \subset ZJU-X102$ .** The synthesized ZJU-X102 was immersed in the CsCl saturated solution. The solution was replenished more than 5 times for 1 day. The crystal data of  $Cs^+ \subset ZJU-X102$  is presented in **Table S5**.

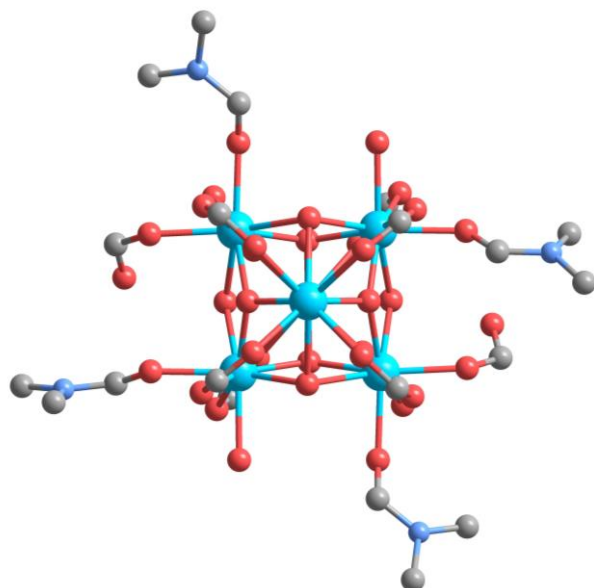
## Materials characterization



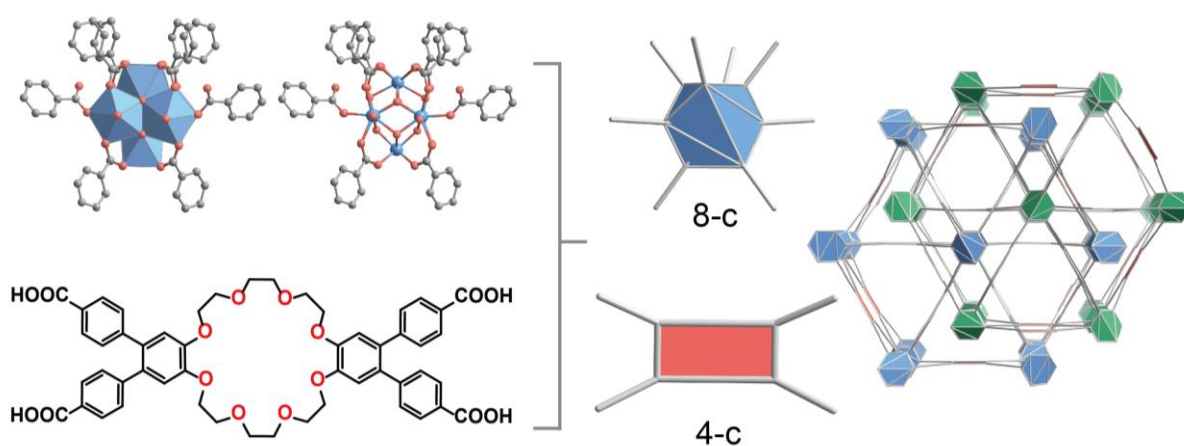
**Figure S1.** 8-connected Zr nodes,  $\text{Zr}_6\text{O}_4(\mu_3\text{-OH})_4(\mu_1\text{-OH})_2(\text{HCOO})_2(\text{H}_2\text{O})_2$  and L1 used in ZJU-X100 (L1 = 4,4',5,5'-terabenzic acid dibenzo-18-crown-6) construct the topology of  $\{4^{20}.6^8\}\{4^6\}_2$ . Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity. Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.



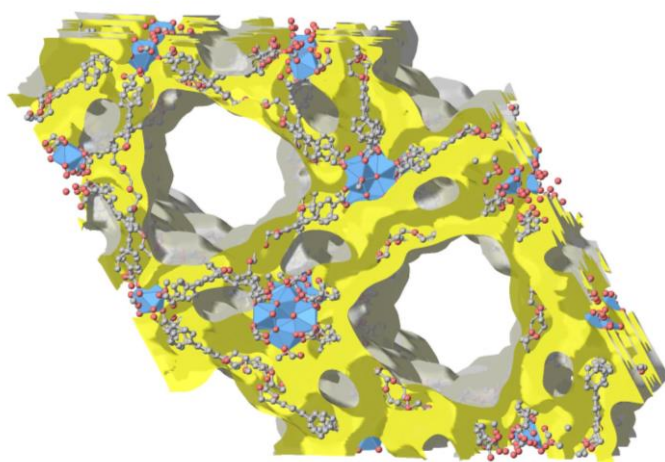
**Figure S2.** The estimated solvent-accessible void volume of ZJU-X100. Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.



**Figure S3.** Coordination mode of  $Zr_6$  node in ZJU-X102. Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.

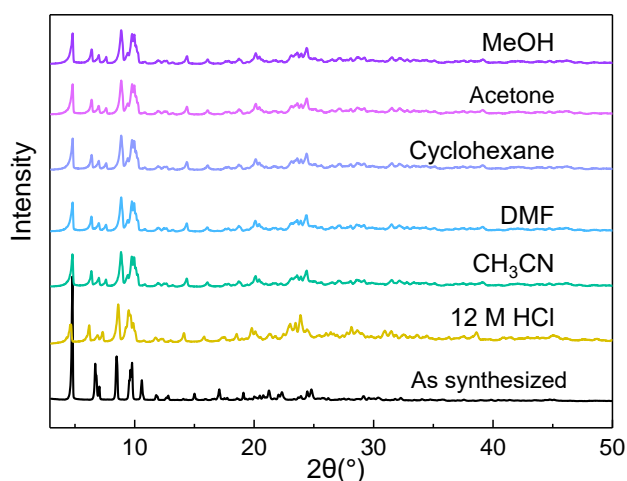


**Figure S4.** 8-connected Zr nodes,  $Zr_6O_4(\mu_3\text{-OH})_4(\mu_1\text{-OH})(\text{HCOO})_2(\text{H}_2\text{O})$  and L2 used in ZJU-X102 (L2 = 4,4',5,5'-terabenzic acid dibenzo-24-crown-8) construct the topology of  $\{4^{14}.6^{11}.8^3\}\{4^3.6^3\}_2$ . Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.



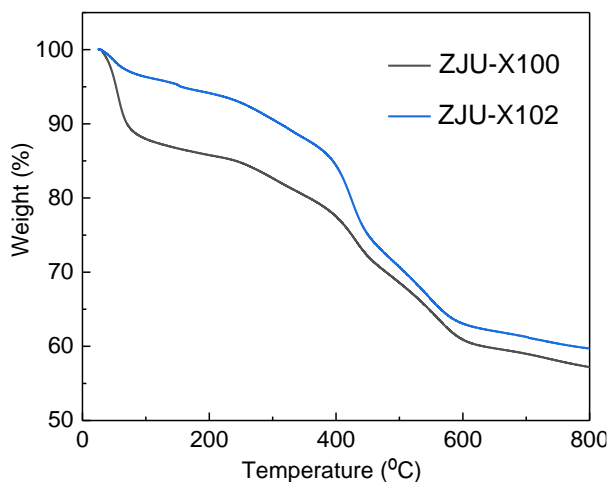
**Figure S5.** The estimated solvent-accessible void volume of ZJU-X102. Atom colors: Zr, ocean blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.

**Hydrolytic and Solvent Stability Measurements.** ZJU-X100 and ZJU-X102 were soaked in NaOH or HCl solution in the pH range from 0 to 11 for 12 h at room temperature. ZJU-X100 were soaked in 12 M HCl solution and solvents with different polarity (MeOH, Acetone, Cyclohexane, DMF, CH<sub>3</sub>CN). The samples were collected and dried for powder X-ray diffraction measurements.



**Figure S6.** Powder X-ray diffraction patterns of ZJU-100 after exposure in different solution.





**Figure S7.** TG curves of ZJU-X100 and ZJU-102.

### Sr<sup>2+</sup> and Cs<sup>+</sup> extraction experiments

**Sorption Kinetics Experiments.** The sorption kinetics experiments were carried by dispersing ZJU-X100 and ZJU-X102 into Sr<sup>2+</sup> and Cs<sup>+</sup> solution with a solid-liquid ratio of 1:1, respectively. The mixture was stirred at room temperature. The supernatant solution was collected by syringe in different time intervals from 1 to 60 min, then filtered by 0.22 μm nylon membrane filters. The filtrates of residual Sr<sup>2+</sup> and Cs<sup>+</sup> were diluted with 5% HNO<sub>3</sub> and the concentrations of Sr<sup>2+</sup> and Cs<sup>+</sup> were determined by ICP-MS. The removal percentages were calculated by the equation as follows:

$$R_e = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  (mg/L) is the initial concentration,  $C_t$  (mg/L) is the concentration of Sr<sup>2+</sup> or Cs<sup>+</sup> after stirring at different times.

**Table S1.** The adsorption kinetics of Sr<sup>2+</sup> and Cs<sup>+</sup> by some typical sorbents compared with ZJU-X100 and ZJU-X102.

Pollutant	Materials	Equilibrium time	Ref
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Strontium	KMS-1	> 2 h	[1]
	Go-Hap	2 h	[2]
	Crown@MPPPs	50 min	[3]
	DCH18C6-functionalized resin	1 h	[4]
	FJSM-SnS	60 min	[5]
	FJSM-InMOF	2040 min	[6]
	SNU-200	360 min	[7]
	MOF-18Cr6	60 min	[8]
	SZ-7	5 min	[9]
	<b>ZJU-X100</b>	<b>1 min</b>	<b>This work</b>
Cesium	KMS-1	5 min (65 °C)	[1]
	KMS-2	10-15 h	[10]
	FJSM-SnS	30 min	[5]
	K-MPS-1	15 min	[11]
	NaFeTiO	200 min	[12]
	Nd-BTC	30 min	[13]
	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ][UO <sub>2</sub> (L <sub>2</sub> )]·0.5DMF·15H <sub>2</sub> O	20 min	[14]
	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sub>4</sub> [(UO <sub>2</sub> ) <sub>4</sub> (TBAPy) <sub>3</sub> ]·22DMF·37H <sub>2</sub> O	20 min	[15]
	AMP-PAN	35 min	[16]
	<b>ZJU-X102</b>	<b>1 min</b>	<b>This work</b>

**Sorption Isotherm Experiments.** The sorption isotherm experiments were measured by exposing ZJU-X100 and ZJU-X102 into different concentrations of Sr<sup>2+</sup> and Cs<sup>+</sup> solution with a solid-liquid ratio of 1:1. The samples were stirred for 12 h at room temperature and filtered by 0.22 μm nylon membrane filters. The concentrations of residual Sr<sup>2+</sup> and Cs<sup>+</sup> in aqueous solution were determined by ICP-MS. The sorption capacity of ZJU-X100 and ZJU-X102 toward Sr<sup>2+</sup> or Cs<sup>+</sup> were calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (2)$$

Where  $C_0$  (mg/L) is the initial concentration,  $C_e$  (mg/L) is the equilibrium concentration,  $m$  (g) is the mass of sorbent, and  $V$  (L) is the volume of the solution.

Langmuir and Freundlich sorption models were used to fit the sorption isotherms. The Langmuir isotherm model is expressed as given below:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

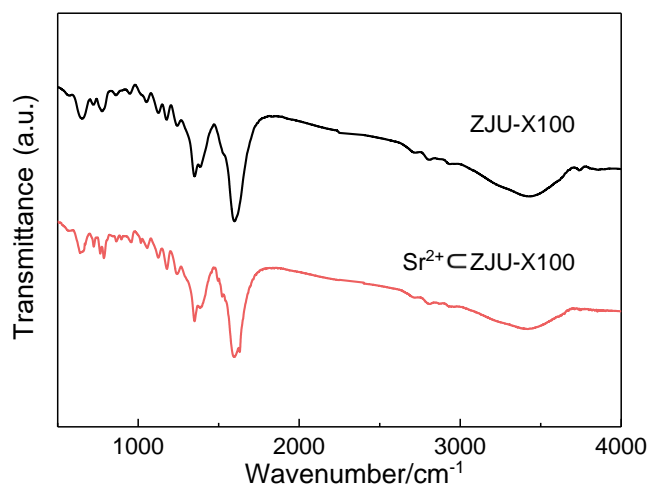
where  $q_e$  (mg/g) is the sorption capacity at equilibrium,  $q_m$  (mg/g) is the maximum sorption capacity and  $K_L$  is the Langmuir constant,  $C_e$  (mg/L) is the equilibrium concentration of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$ . The Freundlich isotherm model is shown as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

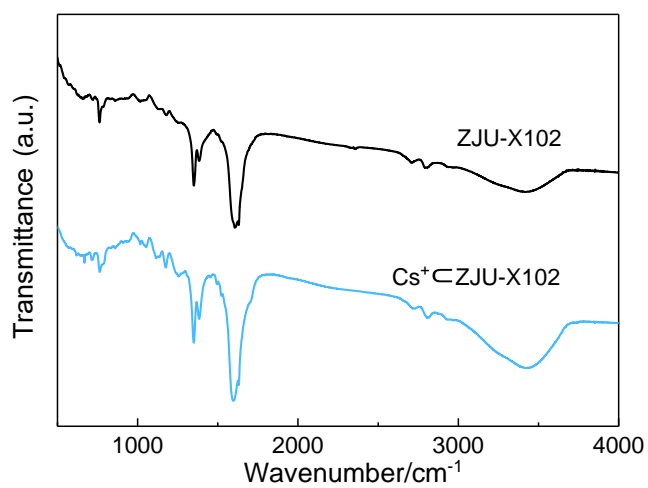
where  $K_F$  is a constant about sorption capacity and  $n$  is related to the intensity of sorption.

**Sorption Selectivity Experiments.** Selectivity experiments of ZJU-X100 and ZJU-X102 toward  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  were performed by adding ZJU-X100 and ZJU-X102 into 10 ppm of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  solution containing corresponding proportions of competing anions with a solid-liquid ratio of 1:1, respectively. The solution was stirred for 12 h at room temperature. The samples were filtered and the concentrations of residual  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  were analyzed by ICP-MS, respectively.

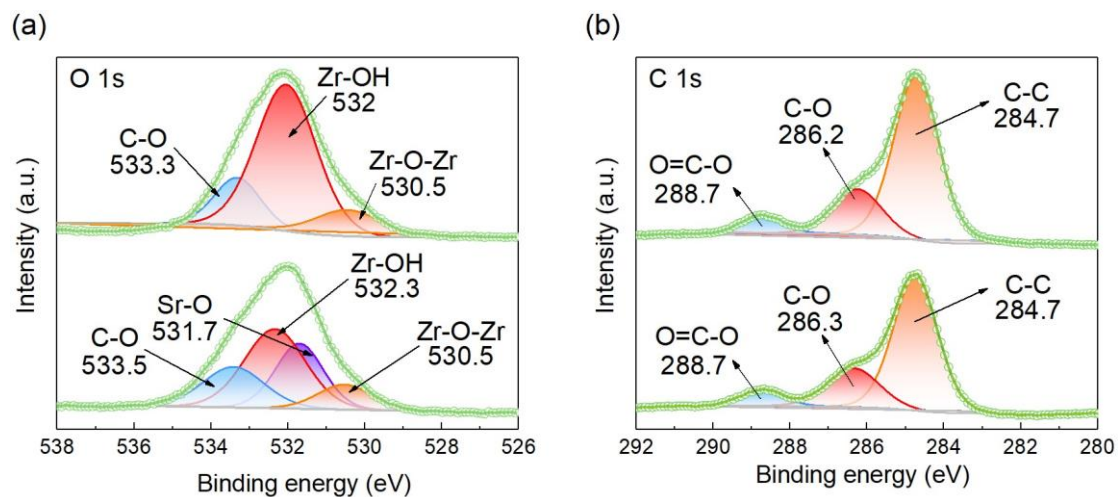
### Sorption Mechanism



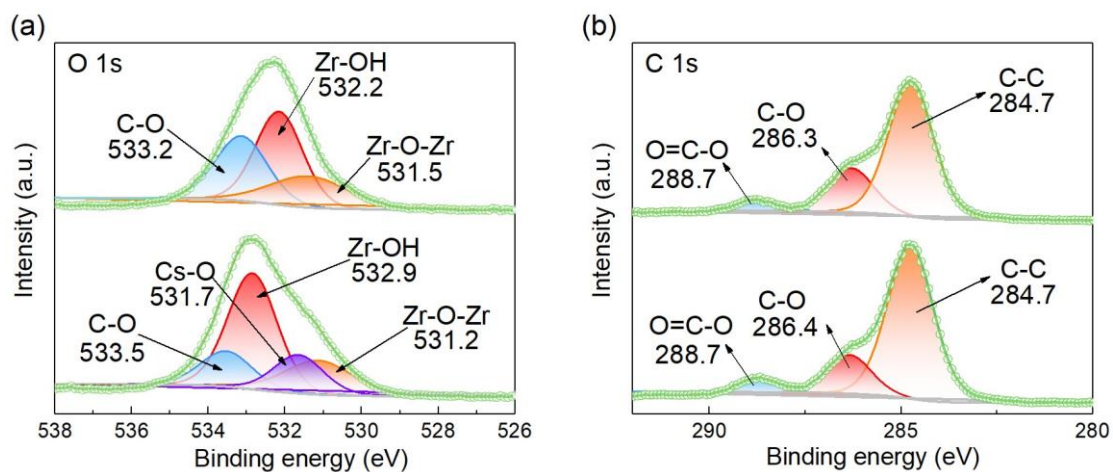
**Figure S8.** FT-IR spectra of ZJU-100 and Sr<sup>2+</sup>@ZJU-100.



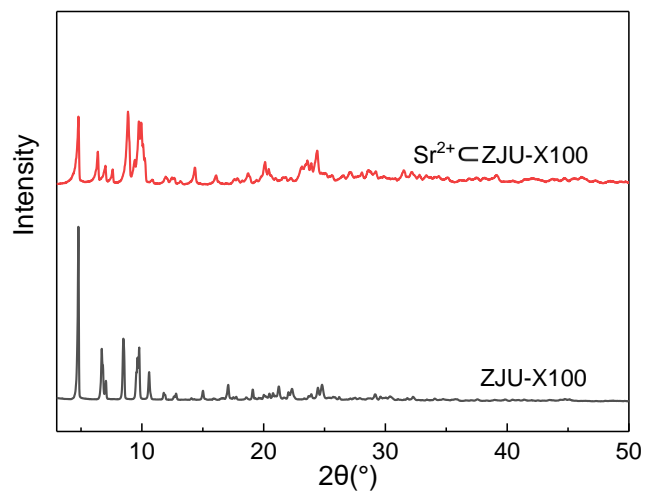
**Figure S9.** FT-IR spectra of ZJU-102 and Sr<sup>2+</sup>@ZJU-102.



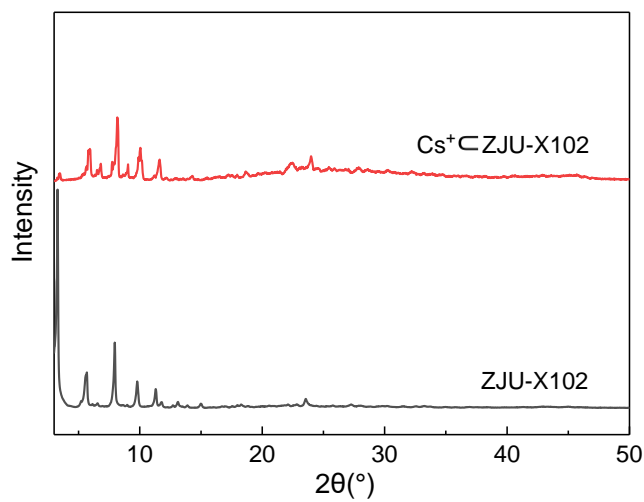
**Figure S10.** High-resolution a) O 1s and b) C 1s spectra of ZJU-X100 before and after  $\text{Sr}^{2+}$  adsorption.



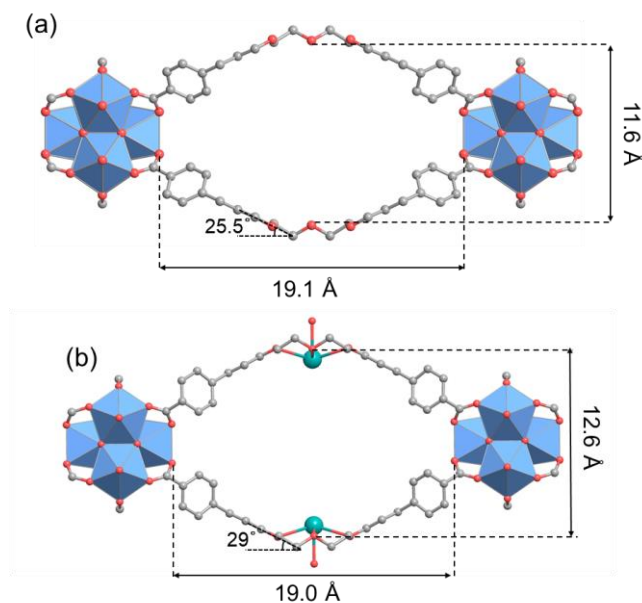
**Figure S11.** High-resolution a) O 1s and b) C 1s spectra of ZJU-X102 before and after  $\text{Cs}^+$  adsorption.



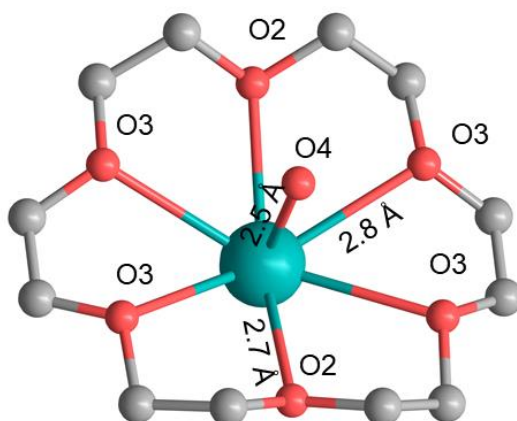
**Figure S12.** Powder X-ray diffraction patterns of ZJU-100 and  $\text{Sr}^{2+}\text{CZJU-100}$ .



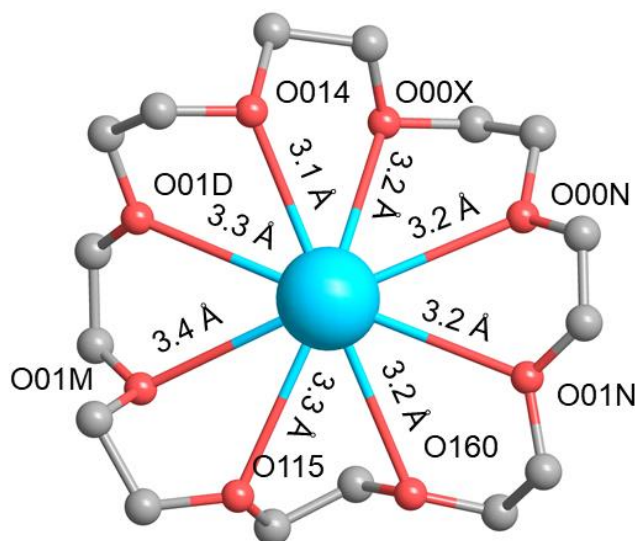
**Figure S13.** Powder X-ray diffraction patterns of ZJU-102 and  $\text{Cs}^{+}\text{CZJU-102}$ .



**Figure S14.** Change of diamond holes of ZJU-X100 a) before and b) after adsorbing Sr<sup>2+</sup>. Atom colors: Zr, ocean blue; Sr, green; O, red; C, light grey. Hydrogen atoms were omitted for clarity.



**Figure S15.** Coordination environment and bond length information of Sr<sup>2+</sup> in 18-crown-6 group of ZJU-X100. Atom colors: Zr, ocean blue; Sr, green; O, red; C, light grey. Hydrogen atoms were omitted for clarity.



**Figure S16.** Coordination environment and bond length information of Cs<sup>+</sup> in 24-crown-8 group of ZJU-X102. Atom colors: Zr, ocean blue; Cs, sky blue; O, red; C, light grey. Hydrogen atoms were omitted for clarity.

**Table S2.** Crystallographic Data and Structure Refinement Parameters of ZJU-X100.

CCDC	2301729
empirical formula	C <sub>98</sub> H <sub>66</sub> O <sub>44</sub> Zr <sub>6</sub>
temperature/K	200.15
fw/(g/mol)	2428.30
cryst syst	orthorhombic
space group	<i>Cmmm</i>
<i>a</i> /Å	26.3044(8)
<i>b</i> /Å	25.7724(12)
<i>c</i> /Å	12.6394(5)
$\alpha$ /deg	90
$\beta$ /deg	90
$\gamma$ /deg	90
volume/Å <sup>3</sup>	8568.6(6)
<i>Z</i>	2
$\rho_{\text{calc}}$ /(g/cm <sup>3</sup> )	0.941



$\mu/\text{mm}^{-1}$	3.361
reflns collected	55082
indep reflns	4205
GOF on $F^2$	1.027
$R_1 [I > 2\sigma(I)]$	0.0788
$wR_2 [I > 2\sigma(I)]$	0.2086

**Table S3.** Crystallographic Data and Structure Refinement Parameters of ZJU-X102.

CCDC	2299622
empirical formula	$\text{C}_{122}\text{H}_{138}\text{N}_6\text{O}_{50}\text{Zr}_6$
temperature/K	193.00
fw/(g/mol)	3035.70
cryst syst	trigonal
space group	$R\bar{3}c$
$a/\text{\AA}$	54.932(3)
$b/\text{\AA}$	54.932(3)
$c/\text{\AA}$	37.744(3)
$\alpha/\text{deg}$	90
$\beta/\text{deg}$	90
$\gamma/\text{deg}$	120
volume/ $\text{\AA}^3$	98636(14)
$Z$	18
$\rho_{\text{calc}}/(\text{g}/\text{cm}^3)$	0.920
$\mu/\text{mm}^{-1}$	1.815
reflns collected	345916
indep reflns	22495
GOF on $F^2$	1.061
$R_1 [I > 2\sigma(I)]$	0.0745
$wR_2 [I > 2\sigma(I)]$	0.2441

**Table S4.** Crystallographic Data and Structure Refinement Parameters of Sr<sup>2+</sup>cZJU-X100.

CCDC	2299617
empirical formula	C <sub>97</sub> H <sub>75.2</sub> O <sub>46</sub> Sr <sub>2</sub> Zr <sub>6</sub>
temperature/K	301.15
fw/(g/mol)	2699.33
cryst syst	orthorhombic
space group	<i>Cmmm</i>
<i>a</i> /Å	27.638(6)
<i>b</i> /Å	26.210(3)
<i>c</i> /Å	11.8556(18)
<i>α</i> /deg	90
<i>β</i> /deg	90
<i>γ</i> /deg	90
volume/Å <sup>3</sup>	8588(2)
<i>Z</i>	2
$\rho_{\text{calc}}$ /(g/cm <sup>3</sup> )	1.044
$\mu$ /mm <sup>-1</sup>	4.135
reflns collected	19009
indep reflns	4156
GOF on <i>F</i> <sup>2</sup>	1.041
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0981
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1231

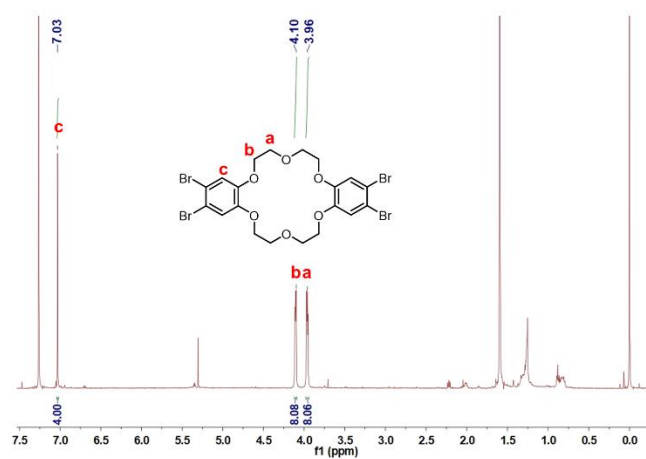
**Table S5.** Crystallographic Data and Structure Refinement Parameters of Cs<sup>+</sup>cZJU-X102.

CCDC	2306608
empirical formula	C <sub>228</sub> H <sub>216</sub> Cs <sub>4</sub> N <sub>6</sub> O <sub>98</sub> Zr <sub>12</sub>
temperature/K	100.00
fw/(g/mol)	6234.33
cryst syst	trigonal

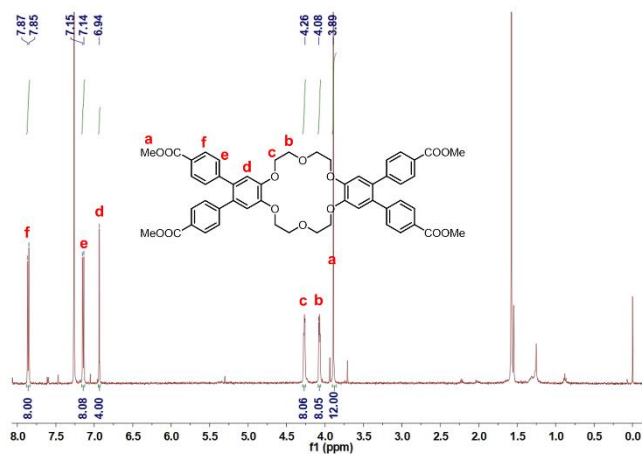
space group	<i>R3c</i>
<i>a</i> /Å	50.9885(5)
<i>b</i> /Å	50.9885(5)
<i>c</i> /Å	37.6460(4)
$\alpha$ /deg	90
$\beta$ /deg	90
$\gamma$ /deg	120
volume/Å <sup>3</sup>	84760.6(19)
<i>Z</i>	9
$\rho_{\text{calc}}$ /(g/cm <sup>3</sup> )	1.099
$\mu$ /mm <sup>-1</sup>	6.106
reflns collected	194778
indep reflns	32606
GOF on $F^2$	1.011
$R_1 [I > 2\sigma(I)]$	0.0768
$wR_2 [I > 2\sigma(I)]$	0.2172

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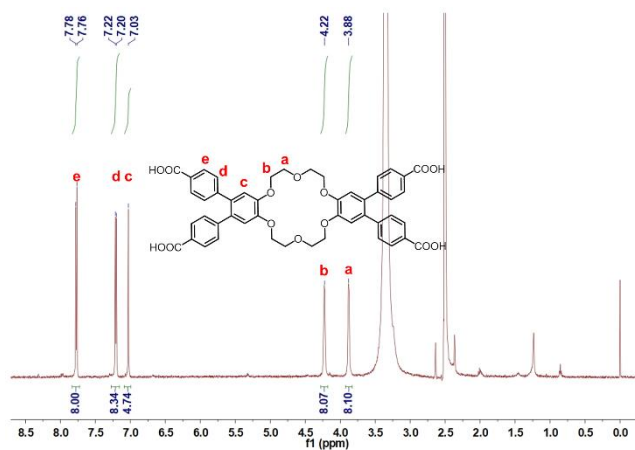
### <sup>1</sup>H NMR Spectra for Compounds



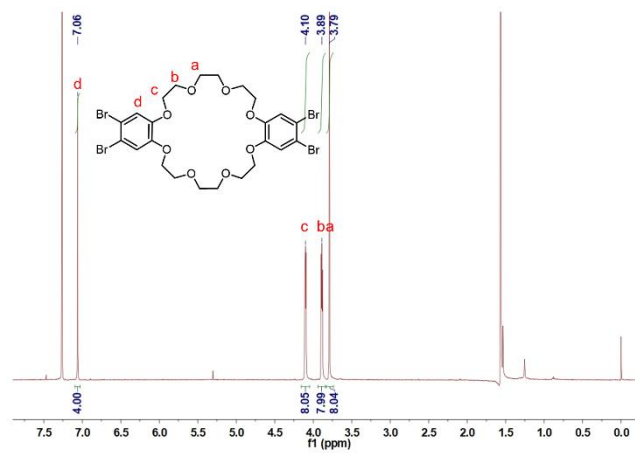
**Figure S17.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-tetrabromodibenzo-18-crown-6. (500 MHz, CDCl<sub>3</sub>, 298 K)



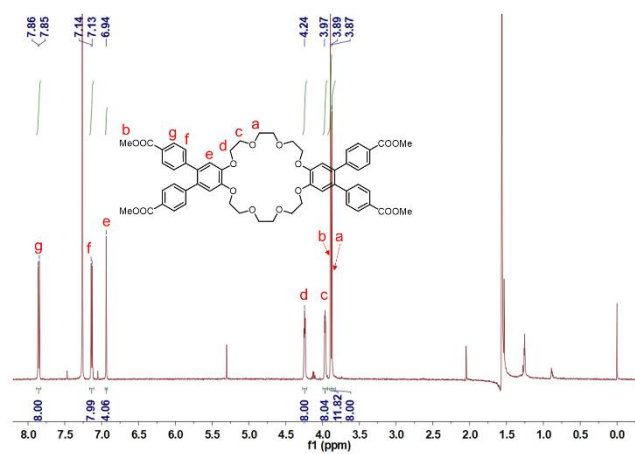
**Figure S18.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-tetrabenzoate dibenzo-18-crown-6. (500 MHz, CDCl<sub>3</sub>, 298 K)



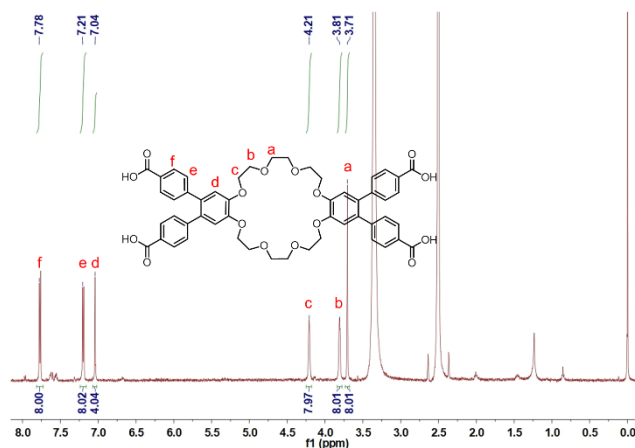
**Figure S19.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-terabenzoic acid dibenzo-18-crown-6. (500 MHz, DMSO-d<sub>6</sub>, 298 K)



**Figure S20.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-tetrabromodibenzo-24-crown-8. (500 MHz, CDCl<sub>3</sub>, 298 K)



**Figure S21.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-tetrabenzoate dibenzo-24-crown-8. (500 MHz, CDCl<sub>3</sub>, 298 K)



**Figure S22.** <sup>1</sup>H NMR spectrum of 4,4',5,5'-terabzoic acid dibenzo-24-crown-8. (500 MHz, DMSO-d<sub>6</sub>, 298 K)

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