# **Supporting Information**

## Water-Stable Hydrazone-Linked Porous Organic Cages

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#### Section S1. General Materials and Measurements

Tetraformylresorcin[4]arene (C4RACHO)<sup>S1</sup> and pentanedioyl dihydrazide<sup>S2</sup> were synthesized by the literature procedures, while other reagent-grade chemicals from commercial sources were employed without further purification. Fourier transform infrared (FT-IR) spectra were recorded in the range 4000–400 cm<sup>-1</sup> with a Magna 750 FT-IR spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were obtained on a Burker AVANCE 400 (400 MHz) for spectrometer. Mass spectra (MS) were recorded on a MaXis™ 4G instrument from Bruker. Data analysis was conducted with the Bruker Data Analysis software (Version 4.0) and simulations were performed with the Bruker Isotope Pattern software. Thermal gravimetric analysis (TGA) was carried out under a dynamic N<sub>2</sub> flow on a NETZSCH STA 449C thermal analyzer by heating samples from 30 to 900 °C. X-ray photoelectron spectroscopy (XPS) was measured on a Thermo ESCALAB 250 spectrometer. Electron paramagnetic resonance (EPR) spectrum was carried out at ambient temperature on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in the X band. UV-vis adsorption spectrum was collected on a PerkinElmer Lambda 350 spectrophotometer at room temperature. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) data for the content of Co and Cu were carried out on an Ultima-2 ICP emission spectrometer. Moreover, CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> adsorption-desorption isotherms of the HPOCs were measured by a Micromeritics ASAP 2020 surface area and porosity analyzer. Before adsorption characterizations, the HPOC samples were degassed at 120 °C in the analysis chamber under vacuum of 10<sup>-5</sup> bar for 12 h. The mixed CO<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> (50:50, v/v) breakthrough separation experiments were measured on a home-built setup coupled with a Pfeiffer GSD320 mass spectrometer. Before measurements, HPOC powder samples were packed into a custom-made stainless-steel column (3.0 mm I.D.×120 mm) with silica wool filling the void space and was activated through sample heating at 100 °C with a constant flow of He (10 mL min<sup>-1</sup>) at room temperature and pressure. He flow was then turned off and the  $CO_2/C_2H_2$  gas flow (2 mL min<sup>-1</sup>) was permitted to pass through the column. By means of mass spectrometer, outlet effluent from the column was continuously monitored. The complete breakthrough of C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> was identified using downstream gas composition reaching that of the feed gas.

#### Section S2. Synthetic Procedures and Characterizations

Synthesis of HPOC-101: C4RACHO (0.025 mmol, 20 mg) and propanedioyl dihydrazide (0.05 mmol, 6.6 mg) were added to DMF (3 mL). The mixture was sealed in a 10 mL glass vial, which was heated at 100 °C for 12 hours. Block crystals were obtained after evaporation of the solution for several hours with yield about 65%. <sup>1</sup> H NMR (400 MHz, DMSO, 298 K):  $\delta$  11.62 (s, 1H), 8.66 (s, 1H), 7.64 (s, 1H), 4.41(t, 1H), 2.18 (t, 2H), 1.38 (m, 1H), 0.94 (d, 6H). ESI–TOF–MS: [M–2H]<sup>2–</sup> calcd. for HPOC-101 (C<sub>108</sub>H<sub>128</sub>N<sub>16</sub>O<sub>24</sub>) is 1015.4571; found 1015.4324.

**Synthesis of HPOC-102.** Synthesis was similar to that of **HPOC-101**, except butanedioyl dihydrazide (0.05 mmol, 7.3 mg) was used instead of propanedioyl dihydrazide. Yield 76%. <sup>1</sup>H NMR (400 MHz, DMSO, 298 K):  $\delta$  11.85 (s, 1H), 8.53 (s, 1H), 7.65 (s, 1H), 4.43 (t, 1H), 2.18 (t, 2H), 1.38 (m, 1H), 0.91 (d, 6H). ESI-TOF-MS: [M-2H]<sup>2-</sup> calcd. for HPOC-102 (C<sub>112</sub>H<sub>136</sub>N<sub>16</sub>O<sub>24</sub>) is 1043.4884; found 1043.4673.

**Synthesis of HPOC-103.** Synthesis was similar to that of **HPOC-101**, except pentanedioyl dihydrazide (0.05 mmol, 8 mg) was used instead of propanedioyl dihydrazide. Yield 74%. ESI–TOF–MS:  $[M-2H]^{2-}$  calcd. for HPOC-103 ( $C_{116}H_{144}N_{16}O_{24}$ ) is 1071.5197; found 1071.4971.

**Synthesis of HPOC-104.** Synthesis was similar to that of **HPOC-101**, except hexanedioyl dihydrazide (0.05 mmol, 8.7 mg) was used instead of propanedioyl dihydrazide. Yield 72%.<sup>1</sup> H NMR (400 MHz, DMSO, 298 K):  $\delta$  11.62 (s, 1H), 8.58 (s, 1H), 7.62 (s, 1H), 4.45 (t, 1H), 2.18 (t, 2H), 1.58 (m, 1H), 0.93 (d, 6H). ESI-TOF-MS: [M-2H]<sup>2-</sup> calcd. for HPOC-104 (C<sub>120</sub>H<sub>152</sub>N<sub>16</sub>O<sub>24</sub>) is 1099.5510; found 1099.5265.

**Synthesis of HPOC-201&301:** Synthesis was similar to that of **HPOC-101**, except m-phthaloyldihydrazide (0.05 mmol, 10 mg) was used instead of propanedioyl dihydrazide. Yield 85% with ratio of **HPOC-201:HPOC-301** about 1:7.<sup>1</sup> H NMR (400 MHz, DMSO, 298 K): δ 12.39 (s, 1H), 8.96 (s, 1H), 8.44 (s, 0.5 H), 8.13 (m, 1 H), 7.71 (m, 1.5 H), 4.55 (t, 1H), 2.18 (t, 2H), 1.38 (m, 1H), 0.99 (d, 6H). ESI-TOF-MS:  $[M-2H]^{2-}$  calcd. for HPOC-201 (C<sub>192</sub>H<sub>204</sub>N<sub>24</sub>O<sub>36</sub>) is 1709.7362; found 1709.7305,  $[M-3H]^{3-}$  calcd. for HPOC-301 (C<sub>256</sub>H<sub>272</sub>N<sub>32</sub>O<sub>48</sub>) is 1519.6536; found 1519.6458.

**Synthesis of HPOC-401:** Synthesis was similar to that of **HPOC-101**, except terephthalohydrazide (0.05 mmol, 10 mg) was used instead of propanedioyl dihydrazide. Yield 70%.<sup>1</sup> H NMR (400 MHz, DMSO, 298 K): δ 11.62 (s, 1H), 9.12 (s, 1 H), 8.16 (m, 2H), 7.74 (s, 1H), 4.41(t, 1H), 2.18 (t, 2H), 1.38 (m, 1H), 0.94 (d, 6H). ESI–TOF–MS: [M–3H]<sup>3–</sup> calcd. for HPOC-401 (C<sub>384</sub>H<sub>408</sub>N<sub>48</sub>O<sub>72</sub>) is 2279.9841; found 2279.9629.

#### Section S3. X-ray Data Collection and Structure Determination

Single-Crystal X-ray Crystallography: All X-ray single crystal data for HPOCs were collected on SuperNova diffractometer equipped with copper micro-focus X-ray source ( $\lambda$  = 1.5406 Å) at 150 K, except that HPOC-401 was measured on XtaLAB Synergy R, HyPix diffractometer equipped with PhotonJet R (Cu) X-ray source ( $\lambda$  = 1.5406 Å) at 100 K. The crystal structures were resolved by direct methods and all calculations were performed on the SHELXTL-2016 program package.<sup>S3</sup> All nonhydrogen atoms were refined anisotropically for the HPOCs, except for HPOC-401 with extra weak crystal diffraction. Thus the non-hydrogen atoms of HPOC-401 were refined isotropically, which have also been observed in other gigantic organic cages.<sup>S4, S5</sup> Hydrogen atoms of the organic ligands were added in the riding model and refined with isotropic thermal parameters. Moreover, most of the DMF solvent molecules can be determine in HPOC-101 to HPOC-104 and HPOC-201. However, the diffuse electron density together with highly disordered solvent molecules of crystallization could not be generated and were not included for HPOCs, thus the crystal structures were treated by the "SQUEEZE" method, <sup>56</sup> a part of the PLATON package of crystallographic software. This had dramatically improved the agreement indices. Moreover, the high  $R_1$  and  $wR_2$  factor for all calix[4] resorcinarene-based organic cages might be due to the weak crystal diffraction, the disorder of the isobutyl groups as well as no heavy atoms in the molecular structure, which are typical, especially for in large organic cage system.<sup>57,</sup> <sup>S8</sup> The detail crystal data and cell parameters for the POCs are summarized in Tables S1 and S2.

	HPOC-101	HPOC-102	HPOC-103	HPOC-104
formula	C <sub>108</sub> H <sub>128</sub>	C <sub>112</sub> H <sub>136</sub>	C <sub>116</sub> H <sub>144</sub>	C <sub>120</sub> H <sub>152</sub>
Tornula	$N_{16}O_{24}$	$N_{16}O_{24}$	$N_{16}O_{24}$	$N_{16}O_{24}$
M / g mol <sup>-1</sup>	2034.2689	2090.3753	2146.4818	2202.5882
т/к	150	150	150	150
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	<i>P</i> -1	C2/c
a / Å	16.5803(6)	15.5926(8)	17.5094(9)	31.8296(3)
b / Å	19.1653(7)	18.0722(8)	17.6077(8)	15.74469(14)
c / Å	28.6484(10)	19.3683(7)	19.7045(11)	39.9084(3)
α (°)	82.336(3)	115.004(4)	95.163(4)	90.0
β (°)	74.654(3)	94.992(4)	107.511(5)	95.2393(8)
γ (°)	83.678(3)	112.026(4)	119.671(5)	90.0
V / ų	8673.79	4385.12	4819.96	19916.4
Z	2	1	1	4
μ (mm <sup>-1</sup> )	0.527	0.598	0.614	0.541
Data measured	57657	28900	33627	48058
Ind. reflns	32323	16575	17278	19116
Parameters	1537	880	1003	917
GOF on F <sup>2</sup>	1.055	1.264	1.421	0.893
R₁ <sup>a</sup> [I →σ(I)]	0.0998	0.1067	0.1175	0.0727
wR <sub>2</sub> <sup>b</sup>	0.2913	0.3005	0.3635	0.2215
CCDC number	2097226	2097227	2097228	2097229

**Table S1.** Crystallographic Data and Structure Refinement for HPOCs

 ${}^{a}R_{1} = \sum \overline{||F_{o}| - |F_{c}|| / \sum |F_{o}|} \cdot {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}$ 

	HPOC-201	HPOC-301	HPOC-401
formula	$C_{192}H_{204}N_{24}O_{36}$	$C_{256}H_{272}N_{32}O_{48}$	$C_{384}H_{408}N_{48}O_{72}$
M / g mol <sup>-1</sup>	3423.8207	4565.0942	6847.6413
т / к	150	150	100
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	C2/c	C2/c	<i>P</i> nnn
a / Å	33.0202(10)	56.553(2)	44.0956(9)
b / Å	65.6703(15)	15.3485(7)	44.5782(8)
<i>c</i> / Å	31.0870(7)	60.220(3)	48.2469(9)
α (°)	90.0	90	90.0
β (°)	106.056(3)	115.851(6)	90.0
γ (°)	90.0	90	90.0
V / ų	64780.9	47040.5	94839.1
Z	4	4	4
μ (mm⁻¹)	0.475	0.368	0.274
Data measured	123881	108538	373277
Ind. reflns	58156	37637	96079
Parameters	2668	1527	1029
GOF on <i>F</i> <sup>2</sup>	1.255	1.123	1.573
R <sub>1</sub> ª [I →σ(I)]	0.1045	0.1279	0.2321
wR <sub>2</sub> <sup>b</sup>	0.3288	0.3742	0.5600
CCDC number	2097230	2097231	2097232

Table S2. Crystallographic Data and Structure Refinement for HPOCs

 ${}^{a}\mathsf{R}_{1} = \sum ||\overline{\mathsf{F}_{o}|} - |\overline{\mathsf{F}_{c}}| / \sum |\overline{\mathsf{F}_{o}}| \cdot {}^{b}\mathsf{w}\mathsf{R}_{2} = \{\sum [\mathsf{w}(\overline{\mathsf{F}_{o}}^{2} - \overline{\mathsf{F}_{c}}^{2})^{2}] / \sum [\mathsf{w}(\overline{\mathsf{F}_{o}}^{2})^{2}]\}^{1/2}$ 

## Section S4. Additional Figures

Section S4a. Additional Figures of HPOCs:



**HPOC-101** 



**HPOC-103** 





**HPOC-401** 







**Fig. S2.** Molecular packing of **HPOC-101** in solid state viewed from [100] direction; hydrogen atoms are omitted for clarity.



**Fig. S3.** Molecular packing of **HPOC-102** in solid state viewed from [010] direction; hydrogen atoms are omitted for clarity.



**Fig. S4.** Molecular packing of **HPOC-103** in solid state viewed from [010] direction; hydrogen atoms are omitted for clarity.



**Fig. S5.** Molecular packing of **HPOC-104** in solid state viewed from [100] direction; hydrogen atoms are omitted for clarity.



**Fig. S6.** Molecular packing of **HPOC-201** in solid state viewed from [100] direction; hydrogen atoms are omitted for clarity.



**Fig. S7.** Molecular packing of **HPOC-301** in solid state viewed from [010] direction; hydrogen atoms are omitted for clarity.



**Fig. S8.** Molecular packing of **HPOC-401** in solid state viewed from [100] direction; hydrogen atoms are omitted for clarity.



Fig. S9. The arrangement of calix[4] resorcinarene units in HPOC-101 to HPOC-104.



**Fig. S10.** The orientation of the phenyl rings (hightlight in green) of the m-phthaloyldihydrazide linkers in **HPOC-201**.



**Fig. S11.** The orientation of the phenyl rings (hightlight in green for vertical direction, and yellow for horizontal direction) of the m-phthaloyldihydrazide linkers in **HPOC-301**.

### Section S4b. FT-IR Spectra of HPOCs:

Comparative study of FT-IR spectra between C4RACHO and **HPOCs** were performed to understand the formation of the organic cages. Notably, the peak around 1642 cm<sup>-1</sup> corresponding to the C=O bond vibration of the C4RACHO transformed to about 1666 cm<sup>-1</sup> for the C=N bond of HPOCs.



Fig. S12. FT-IR spectrum of C4RACHO.



Fig. S13. FT-IR spectrum of HPOC-101.



Fig. S14. FT-IR spectrum of HPOC-102.



Fig. S15. FT-IR spectrum of HPOC-103.



Fig. S17. FT-IR spectrum of HPOC-201&301.



Fig. S18. FT-IR spectrum of HPOC-401.

## Section S4c. <sup>1</sup>H NMR Spectra of HPOCs:

The weak <sup>1</sup>H NMR signals of the HPOCs are ascribed to the solubility of the HPOC samples are low in DMSO- $d_6$ . Moreover, As the solubility of the **HPOC-103** is very low in DMSO- $d_6$ , thus we were unable to characterise it by <sup>1</sup>H NMR.



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 f1 (ppm)

**Fig. S19.** <sup>1</sup>H NMR spectrum of vacuum-dried C4RACHO sample (DMSO-*d*<sub>6</sub>, 400 MHz, 298 K).



**Fig. S20.** <sup>1</sup>H NMR spectrum of vacuum-dried **HPOC-101** sample and its water stability test (DMSO, 400 MHz-*d*<sub>6</sub>, 298 K).



MHz-*d<sub>6</sub>,* 298 K).



**Fig. S22.** <sup>1</sup>H NMR spectrum of vacuum-dried **HPOC-104** sample and its water stability test (DMSO, 400 MHz-*d*<sub>6</sub>, 298 K).



**Fig. S23.** <sup>1</sup>H NMR spectrum of vacuum-dried **HPOC-201&301** sample and its water stability test (DMSO- $d_6$ , 400 MHz, 298 K).



13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 **Fig. S24.** <sup>1</sup>H NMR spectrum of vacuum-dried **HPOC-401** sample and its water stability test (DMSO-*d*<sub>6</sub>, 400 MHz, 298 K).

#### Section S4d. MS spectra of HPOCs:



Fig. S25. MS spectrum of HPOC-101 recorded in DMF.



Fig. S26. MS spectrum of HPOC-102 recorded in DMF.



Fig. S27. MS spectrum of HPOC-103 recorded in DMF.



Fig. S28. MS spectrum of HPOC-104 recorded in DMF.



Fig. S30. MS spectrum of HPOC-301 recorded in DMF.



Fig. S31. MS spectrum of HPOC-401 recorded in DMF.

#### Section S2e. TGA Curves of HPOCs:



Fig. S32. TGA curves of HPOC-101.



Fig. S33. TGA curves of HPOC-102.



Fig. S34. TGA curves of HPOC-103.



Fig. S35. TGA curves of HPOC-104.



Fig. S36. TGA curves of HPOC-201&301.



Fig. S37. TGA curves of HPOC-401.

#### Section S4e. PXRDs of HPOCs:

PXRD analysis showed that all the experimental powder X-ray diffractograms of HPOC samples do not keep their original crystallinity compared to the powder X-ray diffractograms calculated from their single crystal structure data. However, [2+4] HPOCs still kept crystallinity after being taken from mother liquor as well as after adsorption, while the rest larger ones quickly become amorphous. This might be ascribed to that the packing of the isolated cage compounds are assembled by weak supramolecular interactions, which are different to MOFs and COFs assembled with much stronger coordination bonds and covalent bonds, respectively. These phenomena are often observed in cage system, especially for those with large cavities.<sup>S9-S11</sup>



Fig. S38. PXRD patterns of HPOC-101.



Fig. S39. PXRD patterns of HPOC-102.



Fig. S40. PXRD patterns of HPOC-103.



Fig. S41. PXRD patterns of HPOC-104.



Fig. S42. PXRD patterns of HPOC-201&301.



Fig. S43. PXRD patterns of HPOC-401.

#### Section S5. Gas Adsorption Measurements



Fig. S44. N $_2$  adsorption/desorption isotherm of HPOC-101 at 77 K.



Fig. S45.  $N_2$  adsorption/desorption isotherm of HPOC-102 at 77 K.



Fig. S46. N<sub>2</sub> adsorption/desorption isotherm of HPOC-103 at 77 K.



Fig. S47. N<sub>2</sub> adsorption/desorption isotherm of HPOC-104 at 77 K.



Fig. S48. N<sub>2</sub> adsorption/desorption isotherm of HPOC-201&301 at 77 K.



Fig. S49. N<sub>2</sub> adsorption/desorption isotherm of HPOC-401 at 77 K.



Fig. S50. BET-plots of HPOC-101.



Fig. S51. BET-plots of HPOC-102.



Fig. S53. BET-plots of HPOC-104.



Fig. S54. BET-plots of HPOC-201&301.



Fig. S55. BET-plots of HPOC-401.



Fig. S56.  $CO_2$  and  $C_2H_2$  adsorption isotherms of calix[4]resorcinarene at 298 K.



Fig. S57.  $CO_2$  and  $C_2H_2$  adsorption isotherms of HPOC-101 at 298 K.



Fig. S58.  $CO_2$  and  $C_2H_2$  adsorption isotherms of HPOC-103 at 298 K.



Fig. S59.  $CO_2$  and  $C_2H_2$  adsorption isotherms of HPOC-104 at 298 K.



**Fig. S60**. Experimental breakthrough curves of an equimolar mixture of  $CO_2/C_2H_2$  at 298 K and 1 bar over a packed bed of **HPOC-104**.

НРОС-	101	102	103	104	201	301	401
Formula	$C_{108}H_{128}N_{16}O_{24}$	$C_{112}H_{136}N_{16}O_{24}$	$C_{116}H_{144}N_{16}O_{24}$	$C_{120}H_{152}N_{16}O_{24}$	$C_{192}H_{204}N_{24}O_{36}$	$C_{256}H_{272}N_{32}O_{48}$	$C_{384}H_{408}N_{48}O_{72}$
Sp. Gr.	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>C</i> 2/c	<i>C</i> 2/c	<i>C</i> 2/c	<i>P</i> nnn
a (Å)	16.5803(6)	15.5926(8)	17.5094(9)	31.8296(3)	33.0202(10)	56.553(2)	44.0956(9)
b (Å)	19.1653(7)	18.0722(8)	17.6077(8)	15.74469(14)	65.6703(15)	15.3485(7)	44.5782(8)
c (Å)	28.6484(10)	19.3683(7)	19.7045(11)	39.9084(3)	31.0870(7)	60.220(3)	48.2469(9)
α (°)	82.336(3)	115.004(4)	95.163(4)	90.0	90.0	90	90.0
β (°)	74.654(3)	94.992(4)	107.511(5)	95.2393(8)	106.056(3)	115.851(6)	90.0
γ (°)	83.678(3)	112.026(4)	119.671(5)	90.0	90.0	90	90.0
V (ų)	8673.79	4385.12	4819.96	19916.4	64780.9	47040.5	94839.1
R1 (%)	0.0998	0.1067	0.1175	0.0727	0.1045	0.1279	0.2321
CCDC	2097226	2097227	2097228	2097229	2097230	2097231	2097232
WD <sup>[a]</sup> (Å)	5.42	5.60	6.32	6.60	9.66	11.13	9.51
CV <sup>[b]</sup> (Å <sup>3</sup> )	582	656	833	859	1638	3098	6800
CO <sub>2</sub> Ads (mL/g)	154	191	234	207	_[c]	_[c]	231
BET (m <sup>2</sup> g <sup>-1</sup> )	373	563	523	552	_[c]	_[c]	474

**Table S3.** Summary hydrazone-linked HPOCs: crystal data, structure refinement results, window diameters, cavity volumes, CO<sub>2</sub> gas capacities and BET surface areas.

[a] WD stands for window diameter, and [b] CV stands for cavity volume. [c] The CO<sub>2</sub> sorption and BET value for **HPOC-201** and **HPOC-301** mixture is 186 cm<sup>3</sup> g<sup>-1</sup> and 218 m<sup>2</sup> g<sup>-1</sup>.

#### Section S6. Water Pollutants Removal

#### Section S6a. I<sub>3</sub> Pollutant Removal

The iodine solution (0.337 mM) was firstly prepared by dissolving 60 mg nonradioactive iodine and 39.2 mg potassium iodide in 0.7 L deionized water. Adsorption of  $I_{3}$  was accomplished by immersing 3.0 mg adsorbents in 6.0 ml iodine solution and magnetically stirring in a 10 ml glass vial. The suspension was filtered at certain intervals and the filtrate was then detected by UV-vis spectrum.

Moreover, HPOC samples (3.0 mg) was soaked in 6.0 ml KI/I<sub>2</sub> aqueous solution of different concentration (0.6, 0.8, 1.0, 1.2, 1.4 mmol L<sup>-1</sup>). The mixture was stirred for 10 minutes. After filtration, the solution was detected by UV-vis spectrum. The data were fitted to the Langmuir isotherm model  $(c_e/q_e = 1/bq_m + c_e/q_m)$ , where  $q_e$  (mg g<sup>-1</sup>) is the equilibrium adsorption capacity,  $c_e$  (mg L<sup>-1</sup>) is the equilibrium I<sub>3</sub><sup>-</sup> concentration,  $q_m$  (mg g<sup>-1</sup>) is maximum adsorption capacity, b is a Langmuir constant related to the energy of adsorption, representing the affinity between adsorbent and adsorbate.

These HPOCs can be readily regenerated through washing with MeOH at room temperature.



Fig. S61. UV-vis adsorption spectra of the aqueous solutions of I<sub>3</sub><sup>-</sup> at different intervals for HPOC-101.



**Fig. S62**. UV–vis adsorption spectra of the aqueous solutions of  $I_3$ - at different intervals for **HPOC-102**.



**Fig. S63**. UV–vis adsorption spectra of the aqueous solutions of  $I_3^-$  at different intervals for **HPOC-103**.



Fig. S64. UV-vis adsorption spectra of the aqueous solutions of  $I_3^-$  at different intervals for HPOC-104.



**Fig. S65**. UV-vis adsorption spectra of the aqueous solutions of  $I_3^-$  at different intervals for **HPOC-201&301**.



**Fig. S66**. UV-vis adsorption spectra of the aqueous solutions of  $I_3^-$  at different intervals for **HPOC-401**.



**Fig. S67.** Langmuir isotherm of  $I_3^-$  adsorption by **HPOC-101**.

**Table S4.** Characteristic parameters for the adsorption of iodine.

Langmuir model				
<b>q</b> <sub>m</sub> (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	<b>R</b> <sup>2</sup>		
1383	4.522E-3	0.9949		

Table S5. Comparison of adsorption capacities of HPOCs for iodine.

Experimental q <sub>max</sub> (mg g <sup>-1</sup> )	HPOC-101	НРОС-102	HPOC-103	HPOC-104	HPOC-201&301	HPOC-401
	$q_{\rm max} ({\rm mg}~{\rm g}^{-1})$	1305	1294	1257	1203	1193



Fig. S68. XPS spectrum of HPOC-101 after iodine capture.



Fig. S69. EPR spectrum of iodine-loaded HPOC-101.



Fig. S70. Gravimetric iodine uptake of HPOC-101 at 348 K.



Fig. S71. Gravimetric iodine uptake of HPOC-401 at 348 K.

#### Section S6b. Uptake of other pollutants by HPOC-101

In addition to  $I_3^-$ , we have also evaluated the ability of **HPOC-101** to remove other common water pollutants with different size and functionality that span simple aromatics and pharmaceuticals.

Similar to the method mentioned before, 3.0 mg of the adsorbent was stirred in 6.0 ml stock solution (0.1mmol L<sup>-1</sup>). Adsorption studies of each of these pollutants were performed by UV–vis spectroscopy, based on calibration with their measured molar extinction coefficients ( $\epsilon$  in units of M<sup>-1</sup> cm<sup>-1</sup>), which were determined for 2-naphthol (4,639 at  $\lambda_{max} = 273$ nm), 1-naphthyl amine (5,185 at  $\lambda_{max} = 305$ nm), bisphenol A (3,343 at  $\lambda_{max} = 276$  nm), bisphenol S (20,700 at  $\lambda_{max} = 259$ nm), propranolol hydrochloride (5,310 at  $\lambda_{max} = 290$ nm), and 2,4-dichlorophenol (2,255 at  $\lambda_{max} = 284$ nm).

Stock solutions (0.1 mmol L<sup>-1</sup>) of Co (II) and Cu (II) were prepared by dissolving cobalt acetylacetonate and copper chloride dihydrate in deionized water respectively. 3.0 mg of the adsorbent was added in 6.0 ml stock solution. Mixture was stirred for 12 hours followed by filtration to remove the adsorbent and the metal concentrations in the filtrate were determined by ICP-OES.



Fig. S72. UV-vis adsorption spectra of the aqueous solutions of BPA at different intervals for HPOC-101.



Fig. S73. UV-vis adsorption spectra of the aqueous solutions of BPS at different intervals for HPOC-101.



Fig. S74. UV-vis adsorption spectra of the aqueous solutions of PROI at different intervals for HPOC-101.



**Fig. S75.** UV–vis adsorption spectra of the aqueous solutions of 2-NO at different intervals for **HPOC-101**.



**Fig. S76.** UV-vis adsorption spectra of the aqueous solutions of 1-NA at different intervals for **HPOC-101**.



**Fig. S77.** UV–vis adsorption spectra of the aqueous solutions of 2,4-DCP at different intervals for **HPOC-101**.



Fig. S78. UV-vis adsorption spectra of the aqueous solutions of BPS at different intervals for HPOC-401.



**Fig. S79.** UV–vis adsorption spectra of the aqueous solutions of PROI at different intervals for **HPOC-401**.



**Fig. S80.** UV–vis adsorption spectra of the aqueous solutions of 2-NO at different intervals for **HPOC-401**.



**Fig. S81.** UV–vis adsorption spectra of the aqueous solutions of 1-NA at different intervals for **HPOC-401**.



Fig. S82. UV-vis adsorption spectra of the aqueous solutions of 2,4-DCP at different intervals for HPOC-401.

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