Electronic Supplementary Material (ESI) for ChemComm.

A Benzoquinone-Derived Porous Hydrophenazine Framework for Efficient and Reversible Iodine Capture

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1. Experimental Details

1.1. Materials. All the solvents, chemicals and reagents were purchased from Aldrich Chemical Inc., unless otherwise stated. Triptycenehexamine (THA) hexahydrochloride was synthesized according to a procedure described in the literature.[1]

1.2. Methods.

1.2.1. Solution NMR. Solution ^{1}H NMR spectra were recorded at 400.13 MHz using a Bruker Avance 400 NMR spectrometer.

1.2.2. ^{13}C Solid-State NMR. The ^{13}C solid-state NMR spectra were acquired at room temperature on a using a solid-state Varian INOVA 400 MHz. spectrometer. The experiments were performed under magic angle spinning (MAS) at 6.1 kHz with a recycle delay of 3.5 s and using cross polarization (CP) with a ^{13}C radio-frequency (rf) field amplitude of 41 kHz ramped to obtain maximum signal at a ^{1}H rf field of approximately 65 kHz and with an optimized contact pulse of 1.5 ms.

1.2.3. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using a Q5000IR analyzer (TAinstruments) with an automated vertical overhead thermos balance. The samples were heated at the rate of 5 °C min $^{-1}$.

1.2.4. Powder X-ray Diffraction. Laboratory powder X-ray diffraction (PXRD) data were collected in vertical transmission mode geometry on loose samples held on thin Mylar film in aluminum well plates, using a Panalytical Empyrean diffractometer equipped with a high throughput screening XYZ stage, X-ray focusing mirror, PIXcel 3D detector in 1D scanning mode, with Cu-$K\alpha_1$ radiation. PXRD patterns were measured over the 2θ range 5−50°.

1.2.4. Scanning Electron Microscopy. Scanning electron microscope (SEM) images were taken with a Field Emission Scanning Electron Microscope Nanonova 230 FEI, USA.

1.2.5. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV. Samples were mounted on foil since the C1s binding energy was used to calibrate the binding energy shifts of the sample (C1s = 284.8 eV).

1.2.6. UV-Vis Spectra. UV-vis spectra were taken on a PerkinElmer Lambda 35 UV-vis spectrophotometer.

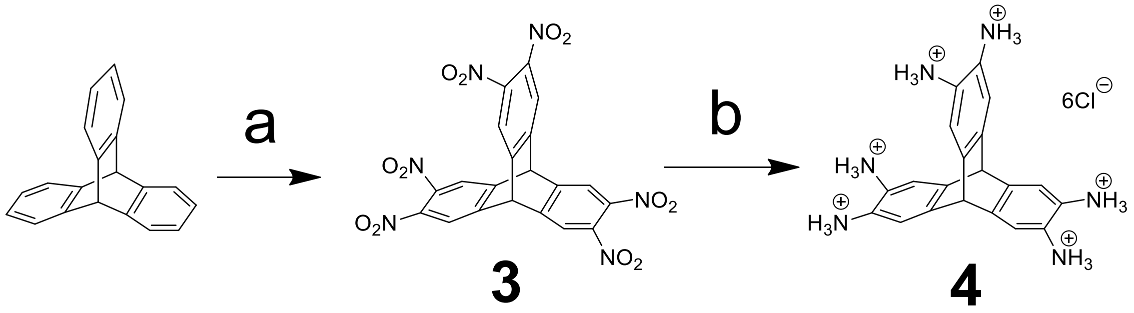
1.2.7. Gas Adsorption Analysis. The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini 2360 surface area analyzer. The CO_2 adsorption and desorption isotherms were measured at 273 K by Autosorb-1-C Quantachrome analyzer. Samples were degassed under dynamic vacuum for 12 h at 150 ^{o}C prior to each measurement.

1.2.8. The Fourier Transform Infrared (FT-IR) Spectroscopy. The FT-IR spectra were recorded from KBr pellets containing ca. 1 mg of the compound in the range 4000-400 cm^{-1} on a Perkin–Elmer one FT-IR spectrophotometer.

2. Synthetic Details

2.1 Synthesis of Triptycenehexaamine (THA) Hexahydrochloride.

Two-step synthesis of air-stable hexaammoniumtriptycene hexachloride **4**.[x]



[x]Key: (a) fuming nitric acid, 85 °C, 4 h; (b) $SnCl_2 \cdot 2H_2O$, EtOH, HCl_{aq} (conc), reflux, 17 h.

Triptycene (5.15 g, 20.2 mol) was suspended in fuming nitric acid (150 mL, 100%) and heated to 85 °C for 4 h. The reaction mixture was cooled to room temperature, poured into water (1 L), and stirred for 1 h. The pale yellow (slightly pink) precipitate was collected by suction filtration, washed with water, and dried in air to give approximately 11 g of crude product. Recrystallization from hot DMF (reflux temperature) gives after cooling to room temperature **3** as yellow crystals (1.85 g, 18%). A suspension of **3** (1.25 g, 2.4 mmol) and tin(II) chloride dihydrate (18 g, 79 mmol) in ethanol (140 mL) and concentrated hydrochloric acid (60 mL) was refluxed for 24 h. The reaction mixture was cooled to room temperature and the white precipitate collected by filtration, washed with concd hydrochloric acid (3 × 15 mL), and dried in vacuum to give **4**$\cdot 7H_2O$ as a pale yellow solid (1.70 g (quant): mp 288 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.04 (s, 6H), 5.32 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.56, 126.04, 116.42, 50.45. The LRESIMS is shown in Fig. S3: *m*/*z* 326.88 [**4**$\cdot 5H_2O + 2H]^{2+}$.

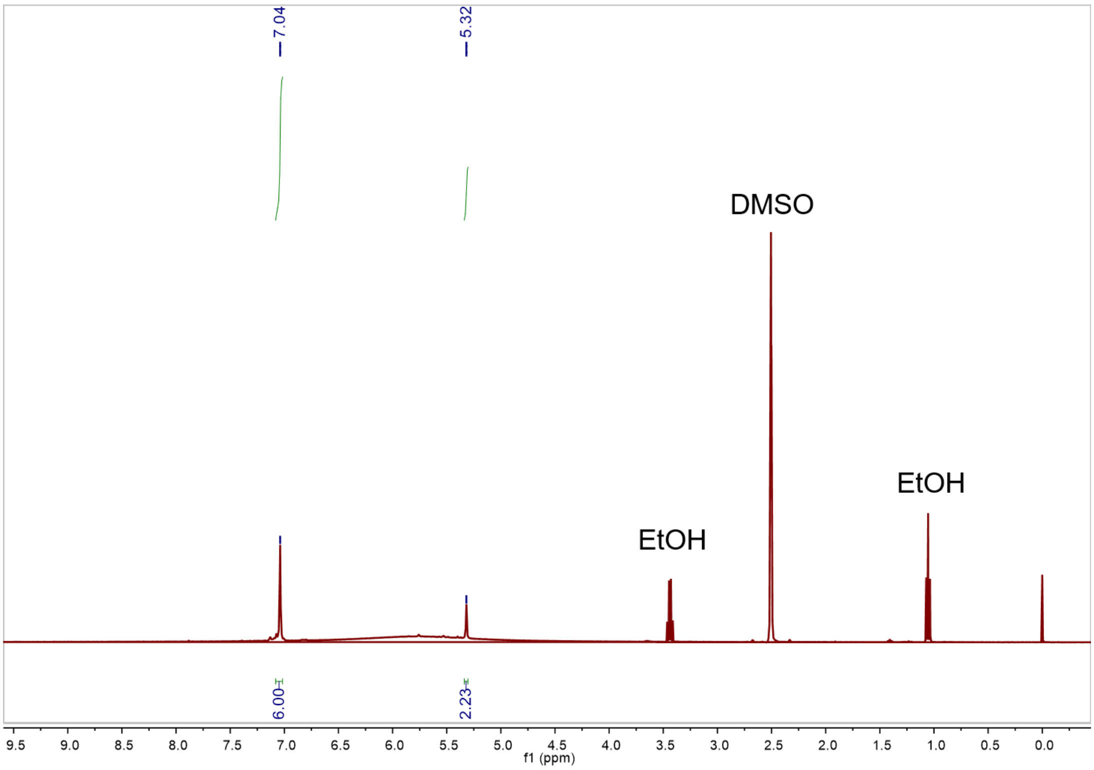


Fig. S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of triptycenehexaamine (THA) hexahydrochloride **4**.

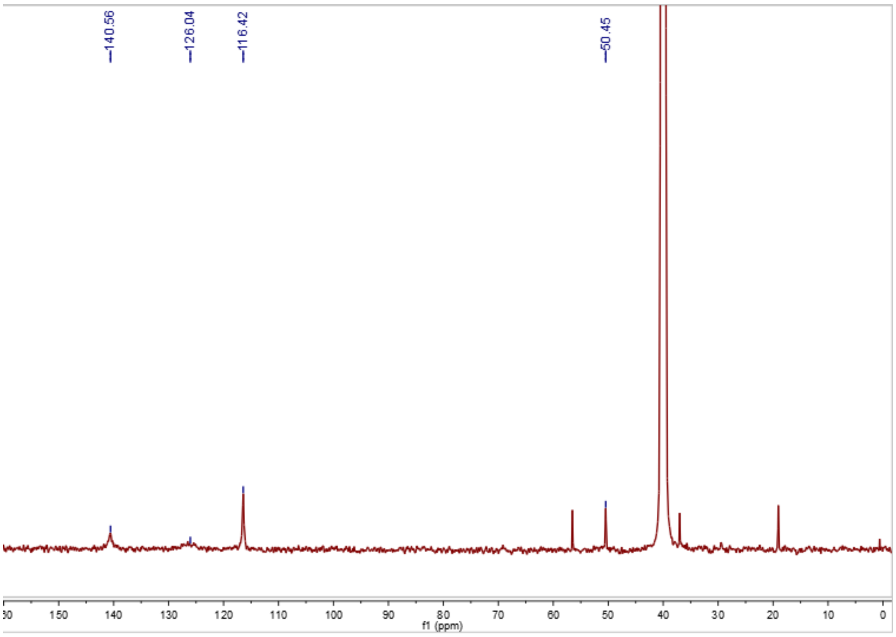


Fig. S2. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, 293 K) of triptycenehexaamine (THA) hexahydrochloride **4**.

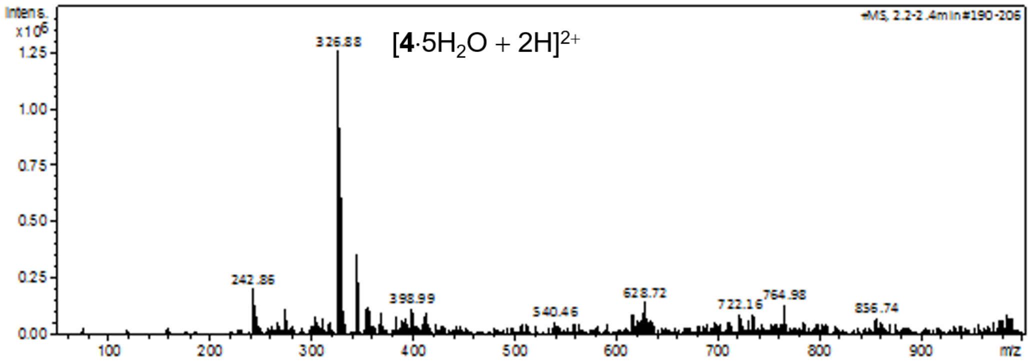
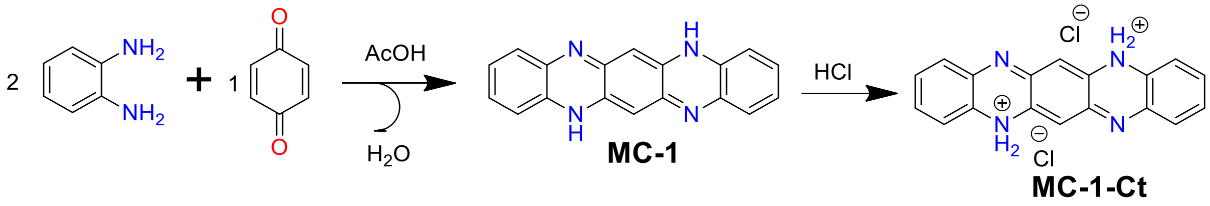


Fig. S3. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, 293 K) of triptycenehexaamine (THA) hexahydrochloride **4**.

2.2 Synthesis of Model Compound MC-1 and MC-1-Ct.



Benzoquinone (1 mmol) was added in a dropwise manner to a solution of *o*-phenylenediamine (2 mmol) in dry AcOH (5 mL) at room temperature, and the mixture was stirred continuously for 20 min.[2] Then the mixture was diluted with ice-cold H_2O (50 mL) and neutralized with sat. aq $NaHCO_3$. The product was extracted with CH_2Cl_2 (3 × 30 mL), and the organic extracts were combined, dried (Na_2SO_4), concentrated in vacuo, and filtered. The residue was purified by flash column chromatography (silica gel, *n*-hexane–ethyl acetate, 90:10 to 40:60) to give the model compound **MC-1**. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.87-7.89 (m, 4H), 7.53-7.55 (m, 4H), 6.89 (s, 2H), 6.27 (s, 2H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 146.40, 143.73, 141.20, 128.53, 128.07. The LRESIMS is shown in Fig. S6: *m*/*z* 282.93 [**MC-1** – H]$^-$. Model compound **MC-1** (5 mg) was then dissolved in diluted HCl (2 mL, 1 M). The removal of HCl gave to the positively-charged model compound **MC-1-Ct**. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.06-8.08 (m, 4H), 7.73-7.75 (m, 4H), 7.05 (s, 2H).

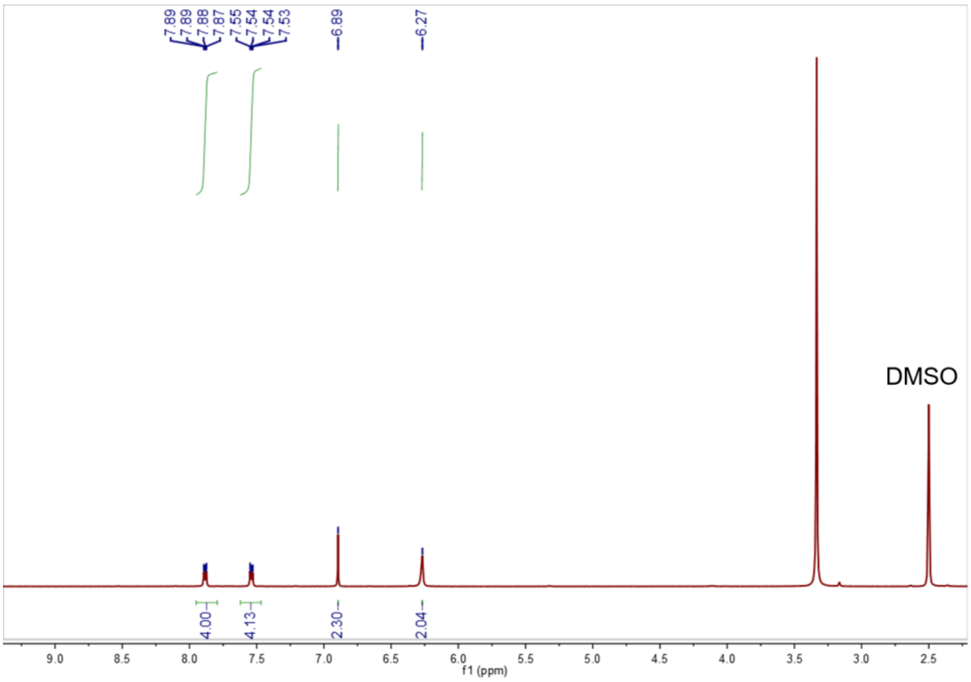


Fig. S4. ^{1}H NMR spectrum (400 MHz, DMSO-*d*$_6$, 293 K) of model compound **MC-1**.

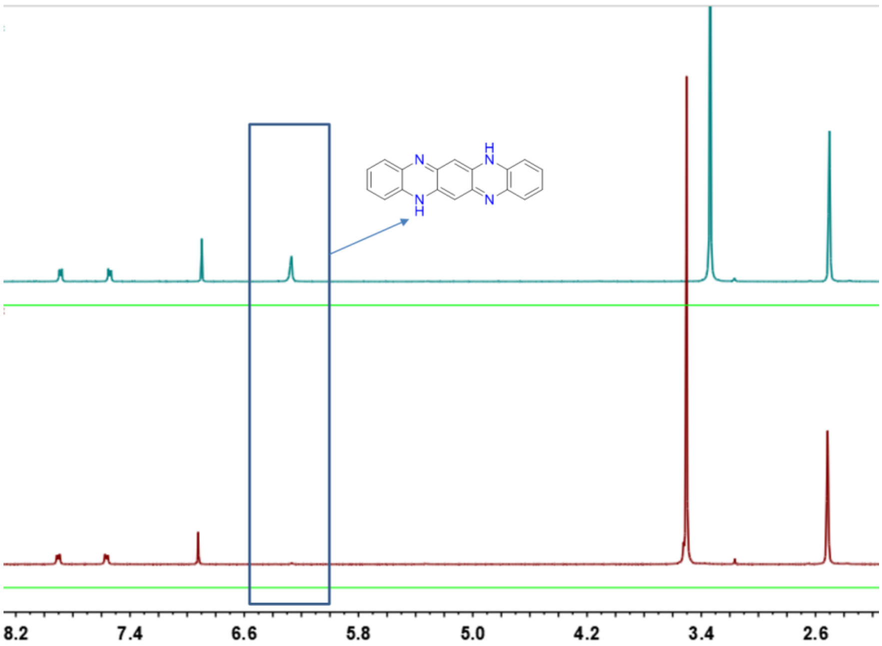


Fig. S5. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K): model compound **MC-1** (top); model compound **MC-1** in the presence of a drop of D_2O (bottom).

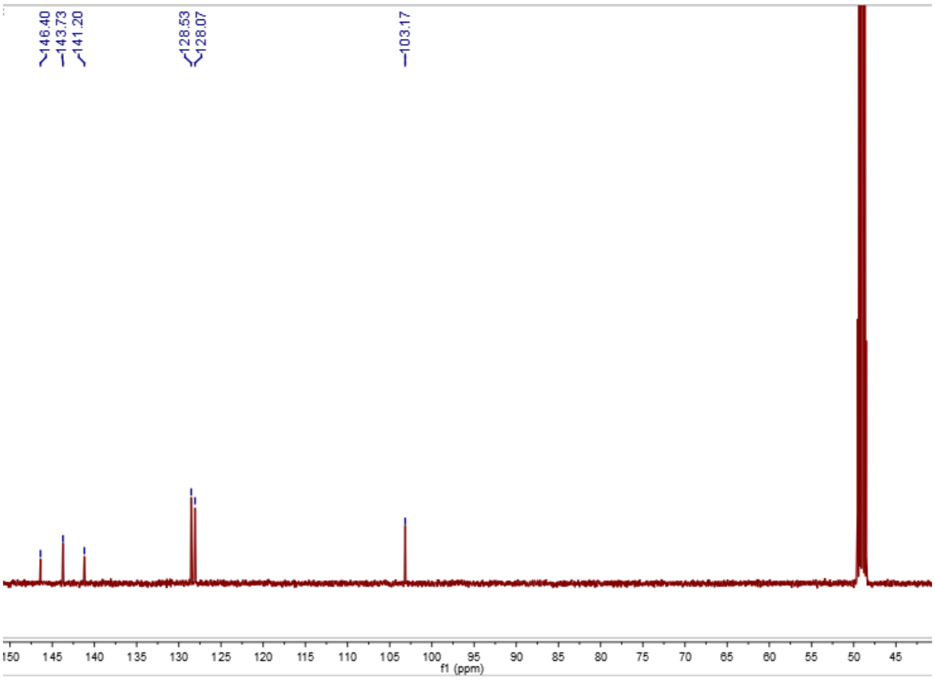


Fig. S6. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, 293 K) of model compound **MC-1**.

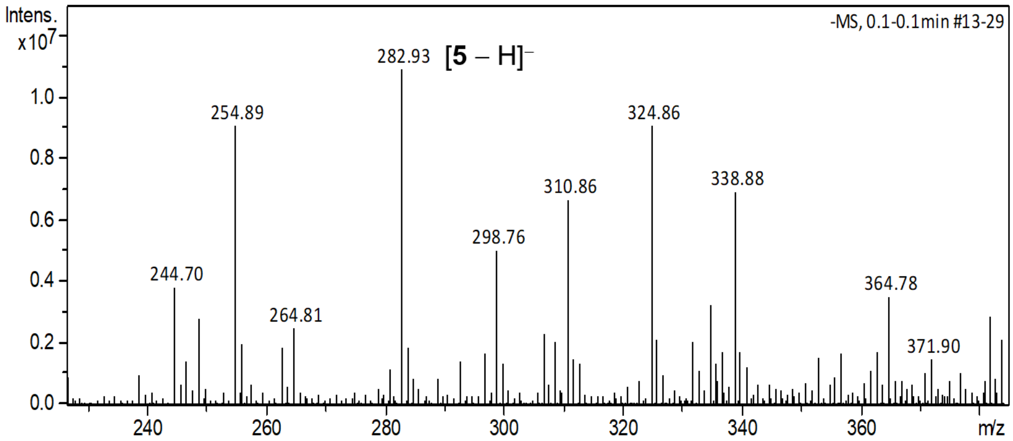


Fig. S7. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, 293 K) of model compound **MC-1**.

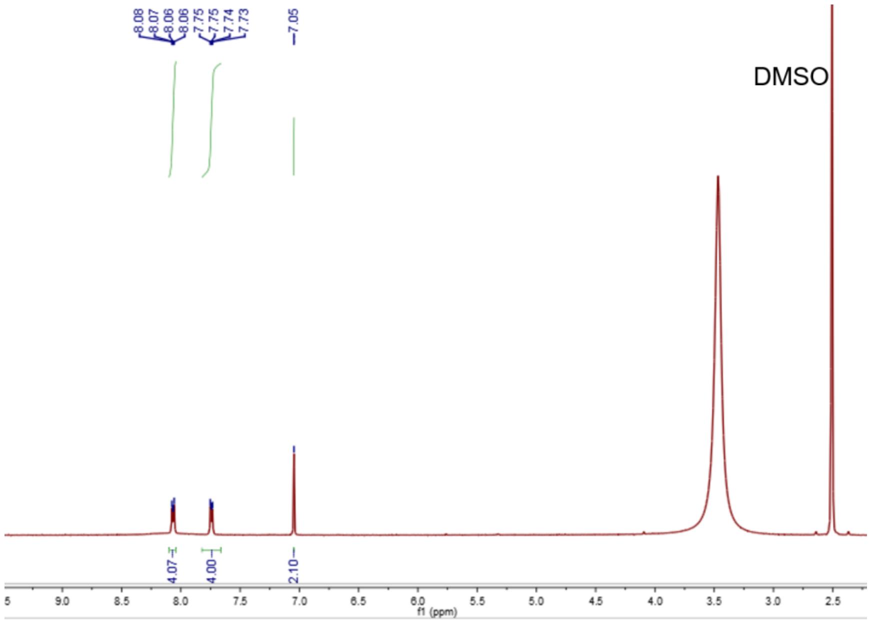


Fig. S8. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of model compound **MC-1-Ct**.

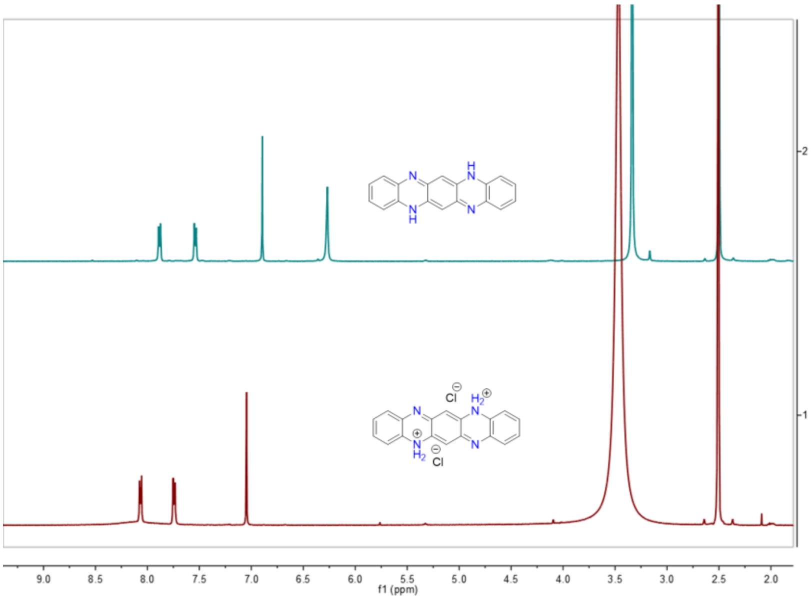
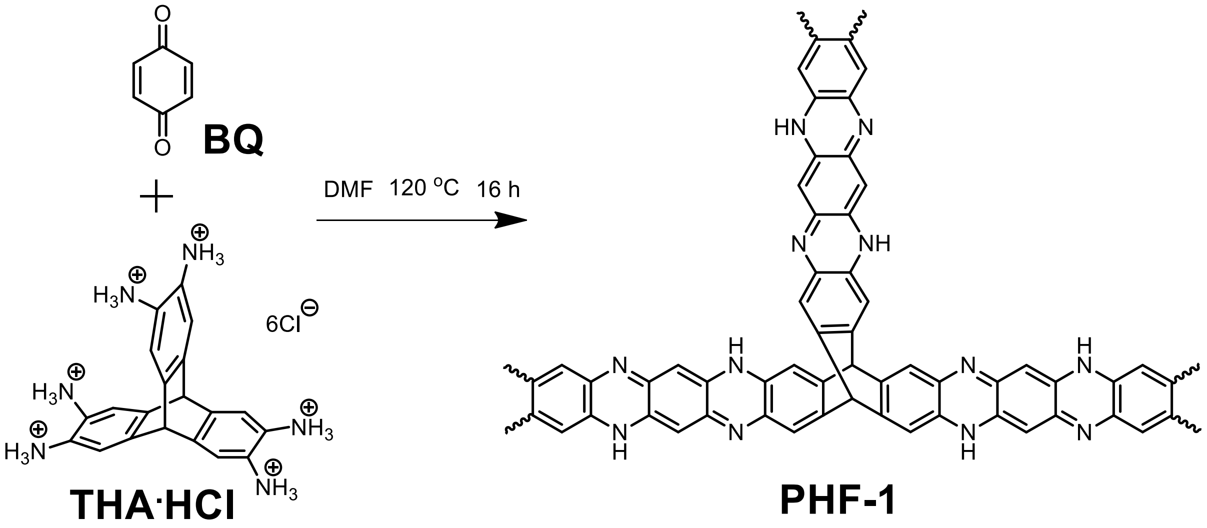


Fig. S9. Comparison of ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of model compound **MC-1** (top) and positively-charged model compound **MC-1-Ct** (bottom).

2.3 Synthesis of Porous Hydrophenazine Framework (PHF-1)



Triptycene hexamine (THA) hexahydrochloride (216 mg) were charged into a 20 mL vial where dry DMF (8 mL) were added. The vial was violently agitated for complete dissolution of THA. Benzoquinone (54 mg) was then added dropwise to the solution with stirring at room temperature. After completion of addition of benzoquinone, the stirring was stopped and the vial was then heated at 120 °C with the lid loose. Dark-red precipitates were collected by filtration after 16 h and washed with sat. aq $NaHCO_3$ and methanol. After that, a Soxhlet extraction with water and methanol for 1 day each was carried out. The sample was dried at 50 °C under reduced pressure (0.01 mmHg) overnight to afford dark-red powder in a yield of 88%.

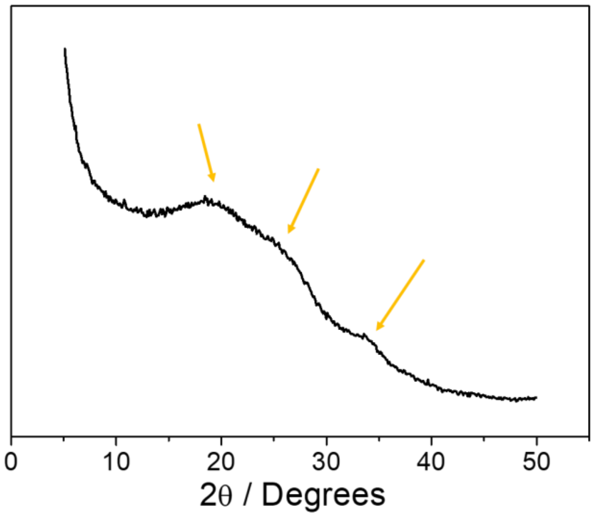
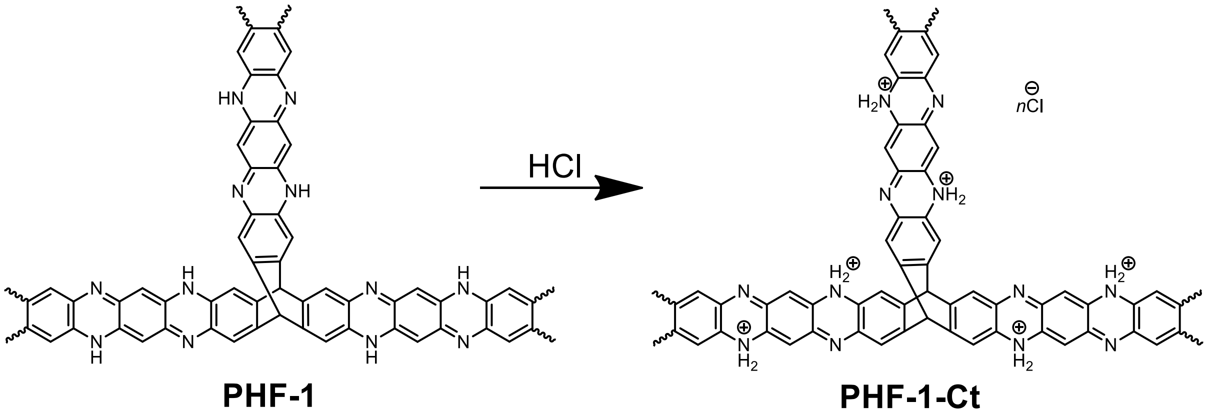


Fig. S10. Powder X-ray diffraction (PXRD) pattern of **PHF-1**.

2.4 Synthesis of Positively-Charged Porous Hydrophenazine Framework (PHF-1-Ct)



PHF-1 (25 mg) was added to 20 mL diluted HCl (1 M). The resultant turbid solution was kept stirring for 30 min. Dark-red precipitates were collected by filtration. The sample was dried at 60 °C under reduced pressure (0.01 mm Hg) overnight to afford dark-red powder in a quantitative yield.

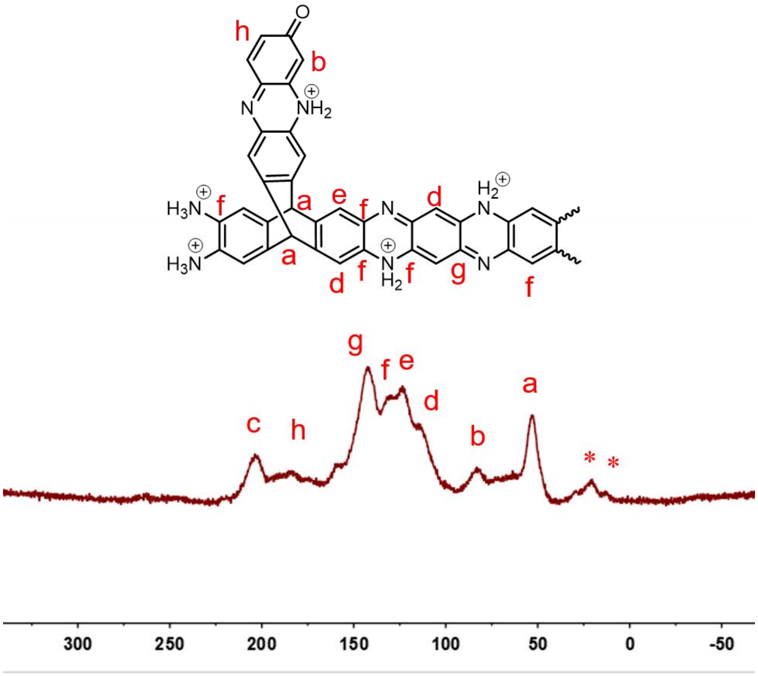


Fig. S11. Solid state ^{13}C-CP/MAS NMR spectrum of **PHF-1-Ct**.

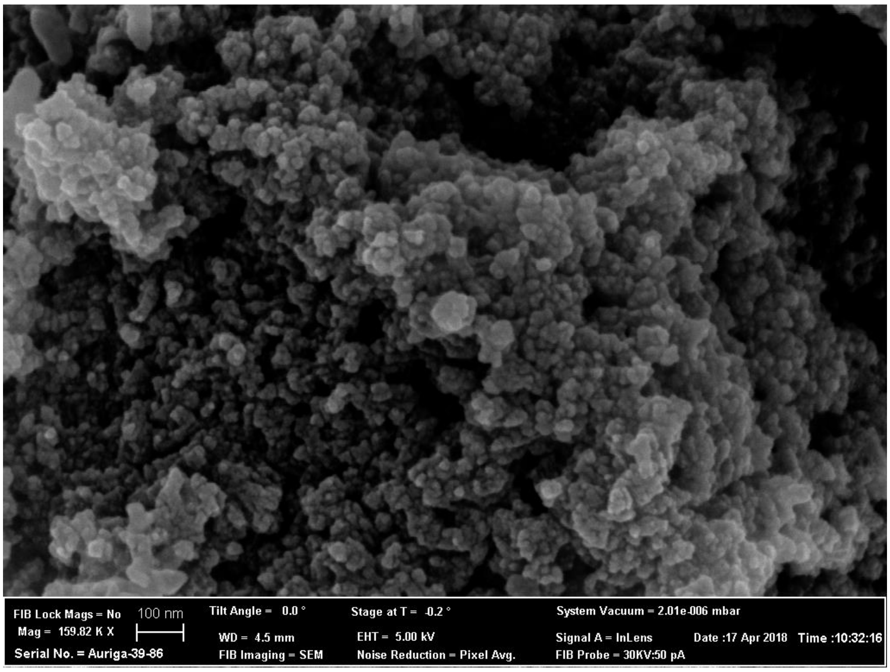


Fig. S12. (a) FE-SEM image of **PHF-1-Ct**.

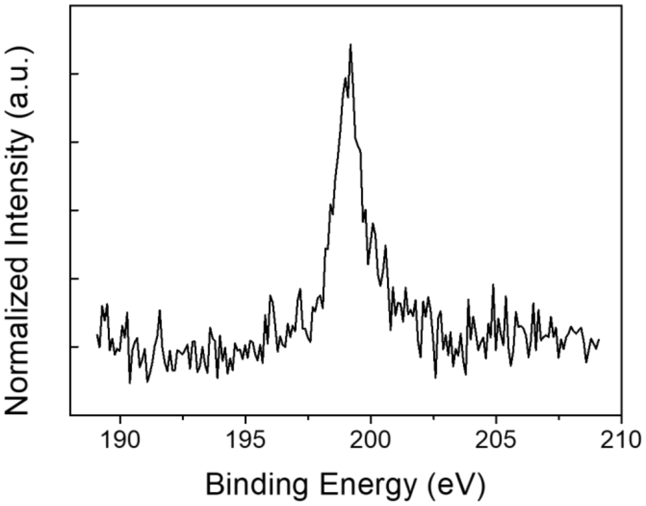


Fig. S13. Cl 2p XPS spectrum of **PHF-1-Ct**.

3. Iodine Capture Experiments

3.1 Iodine Vapor Capture Experiments

An open small vial (2.0 mL) containing the **PPF** sample (50 mg) was placed in a large vial (10 mL) containing iodine (2.0 g). The large vial was sealed and kept in an oven at 70 °C. After a certain period, the large vial was cooled to room temperature. The small vial containing the **PPF** sample was weighed and placed back into the iodine-containing large vial. The large vial was sealed and put back in the oven at 70 °C to continue the adsorption till the mass of the small vial containing the **PPF** sample did not change.

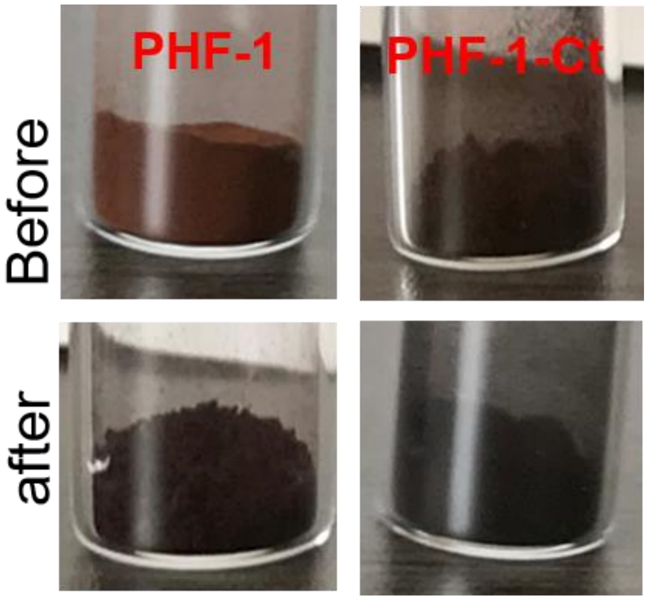


Fig. S14. Photographs showing the color change when 50 mg of **PHF-1** or **PHF-1-Ct** were exposed to iodine vapor.

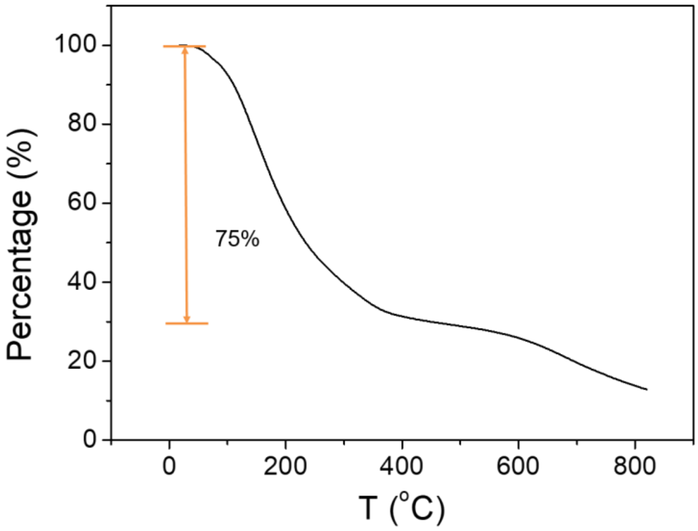


Fig. S15. TGA curves of **PHF-1** after adsorption of iodine vapor for 24 h.

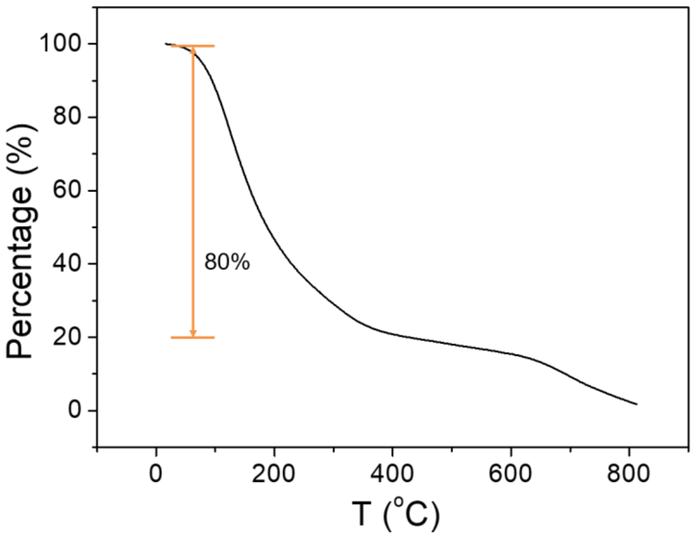


Fig. S16. TGA curves of **PHF-1-Ct** after adsorption of iodine vapor for 24 h.

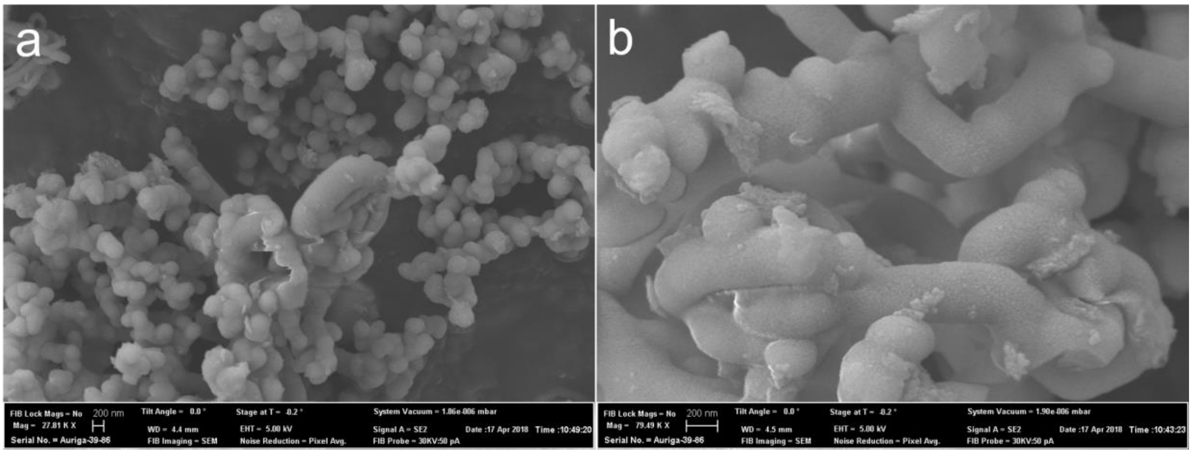


Fig. S17. SEM images of (a) **PHF-1** and (b) **PHF-1-Ct** after adsorption of iodine vapor.

3.2 Iodine Capture in Solutions

PPF-1-Ct (3.0 mg) was added to an iodine solution (20.0 mM, 2 mL) with shaking. The UV-Vis spectrum of the solution was recorded over time.

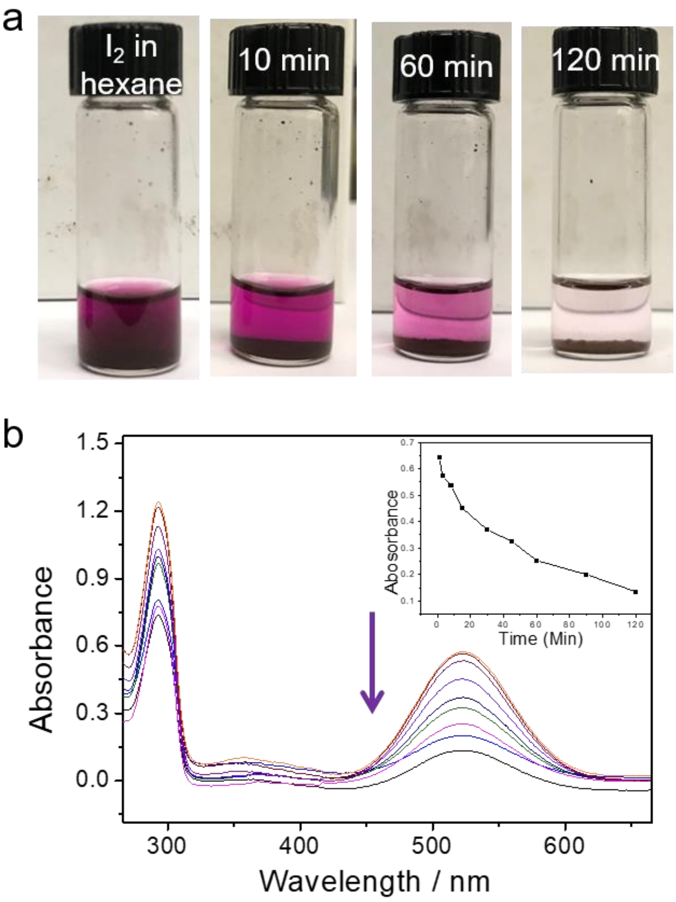


Fig. S18. (a) Photographs and (b) time-dependent UV/vis absorption spectra when 25 mg of **PHF-1-Ct** were placed in 2 mL iodine *n*-hexane solution.

3.2 Iodine Release and Recyclability of PHFs

Iodine-loaded **PHF-1** and **PHF-1-Ct** were immersed in ethanol to release the adsorbed iodine. After 5 hours, the resultant **PHF-1** and **PHF-1-Ct** were collected by filtration, washed with ethanol three times and dried under vacuum at 80 °C over 24 h.

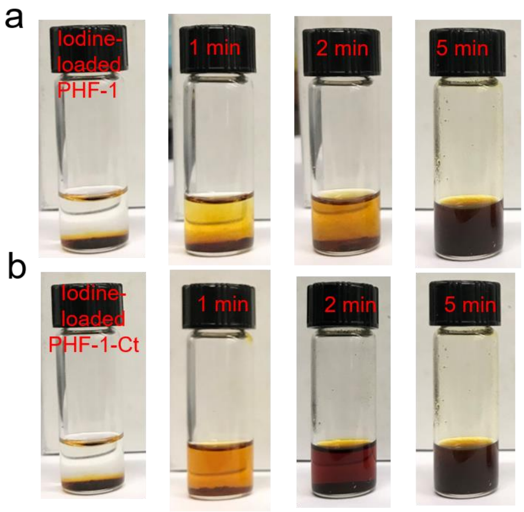


Fig. S19. Iodine release from (a) iodine-loaded **PHF-1** and (b) iodine-loaded **PHF-1-Ct** in ethanol.

Table S1. Summary of the iodine adsorption capacity, releasing efficiency and recyclability of reported materials.

	Material name	Temp (°C)	Solvent or I_2 vapor	Capacity (g/g)	Release solvent	Release efficiency	Recyclability	Reference
Zeolites	Ca-zeolite A	25	I_2 vapor	0.04	water	4.9%	n.r.	*ACS Appl. Mater. Interfaces*, **2009**, *1*, 1579
	Ag+-MOR	75	I_2 vapor	0.16	n.r.	n.r.	n.r.	*Ind. Eng. Chem. Res.* **2017**, *56*, 2331
Activated charcoals	AC1, AC2	75	I_2 vapor	1.05-1.17	n.r.	n.r.	n.r.	*Ind. Eng. Chem. Res.* **2017**, *56*, 2331
Ionic liquids	DESs	25	cyclohexane	0.48-0.99	n.r.	n.r.	n.r.	*Green Chem.*, **2016**, *18*, 2522
	[Bmim][Br]	25	cyclohexane	2.1	n.r.	n.r.	n.r.	*Phys. Chem. Chem. Phys.*, **2014**, *16*, 5071
Silver-based Adsorbents	AC-6120-silver impregnated silica gel	130	I_2 vapor	0.135	n.r.	n.r.	n.r.	*Methods of Gas Phase Capture of Iodine from Fuel Reprocessing Off-Gas: A Literature Survey*, INL/EXT-07-12299, Idaho National Laboratory: Idaho Falls, ID, 2007.
	AgA-silver impregnated alumina	150	I_2 vapor	0.10-0.24	n.r.	n.r.	n.r.	
	AgZ-silver exchanged mordenite	150	I_2 vapor	0.17	n.r.	n.r.	n.r.	
Resins	Amberlite XAD series	<50	I_2 vapor	0.2-1.0	n.r.	n.r.	n.r.	
MOFs	MIL series, CAU-1	25	cyclohexane	Up to 0.31	ethanol	40%-70%	n.r.	*Chem. Commun.*, *2013*, *49*, *10320*
	$Zn_9(btc)_4(atz)_{12}$	25	cyclohexane	0.40	ethanol	n.r.	n.r.	*Inorg. Chem.* **2016**, *55*, 13035
	Complex 1′	25	cyclohexane	1.01	ethanol	100%	n.r.	*J. Am. Chem. Soc.* **2010**, *132*, 2561
	CdL_2	25	Cyclohexane / I_2 vapor	0.18 / 0.46	ethanol	98%	n.r.	*Chem. Commun.*, **2011**, *47*, 7185
	$\{[(ZnI_2)_3(TPT)_2]\cdot 5.5(C_6H_5NO_2)\}_n$	25	I_2 vapor	1.73	irreversible capture		no	*Chem. Sci.*, **2017**, *8*, 3171
	Zr–stilbene MOF	25	I_2 vapor	2.79	Physi- and chemisorption		n.r.	*Chem. Eur. J.* **2016**, *22*, 4870
	Cu-BTC	75	I_2 vapor	1.75	n.r.	n.r.	n.r.	*Chem. Mater.* **2013**, *25*, 2591
	$[Zn_2(tptc)(apy)_{2-x}(H_2O)_x]\cdot H_2O$	75	I_2 vapor	2.16	ethanol	n.r.	n.r.	*Inorg. Chem.* **2016**, *55*, 9270
	ZIF-8	77	I_2 vapor	1.25	n.r.	n.r.	n.r.	*J. Am. Chem. Soc.* **2011**, *133*, 12398

	$\{[Cu_6(pybz)_8(OH)_2]\ I^{5-}\ I^{7-}\}n$		Cocrystallization	0.76	methanol	n.r.	n.r.	*J. Am. Chem. Soc.* **2012**, *134*, 4857
Porous polymers or organic materials	CC3	20	I_2 vapor	0.558	ethanol	n.r.	n.r.	*J. Am. Chem. Soc.* **2011**, *133*, 14920
	CMPN	70	I_2 vapor	0.97-2.08	ethanol	n.r.	n.r.	*J. Mater. Chem. A*, **2015**, *3*, 87
	PAF-23-25	75	I_2 vapor	up to 2.76	ethanol	n.r.	n.r.	*Angew. Chem. Int. Ed.* **2015**, *54*, 12733
	BDP-CPP-1	75	I_2 vapor	2.83			n.r.	*J. Mater. Chem. A*, **2017**, *5*, 6622
	NiP-CMP	77	I_2 vapor	2.02	ethanol	96%	n.r.	*Chem. Commun.*, **2014**, *50*, 8495
	Azo-Trip	77	I_2 vapor	2.33	ethanol	96.4%	5 cycles	*Polym. Chem.*, **2016**, *7*, 643
	AzoPPN	77	I_2 vapor / cyclohexane	2.90	hexane	~99%	n.r.	*Chem. Eur. J.* **2016**, *22*, 11863.
	SCMP-I and SCMP-II	80	I_2 vapor	3.45/3.24	Physi- and chemisorption hexane	~60%	n.r.	*Chem. Commun.*, **2016**, *52*, 9797
	HCMPs	85	I_2 vapor	3.16	heating	98.8%	3 cycles	*Macromolecules*, **2016**, *49*, 6322
	EtP6	70	I_2 vapor / water, *n*-hexane	0.2	cyclohexane	100%	5 cycles	*J. Am. Chem. Soc.* **2017**, *139*, 15320
	CalPn-Li		I_2 vapor / *n*-hexane	up to 3.12	ethanol	n.r.	3 cycles	*Chem. Mater.* **2017**, *29*, 8968
	HCOF-1	75	I_2 vapor /Water	2.9 ± 0.1	DMSO	80%	4 cyles	*J. Am. Chem. Soc.* **2017**, *139*, 7172
	TPB-DMTP COF/ TTA-TTB COF	77	I_2 vapor	6.2	methanol	97%	5 cycles	*Adv. Mater.* **2018**, DOI: 10.1002/adma.201801991
	PHF-1-Ct/PHF-1	70	I_2 vapor / water, *n*-hexane	4.05/3.05	ethanol	~99%	5 cycles	This work

References

1. M. Mastalerz, S. Sieste, M. Ceni and I. M. Oppel, *J. Org. Chem.*, 2011, **76**, 6389.
2. H. Kour, S. Paul, P. P. Singh and R. Gupta, *Synlett*, 2014, **25**, 495.