Electronic Supplementary Information (ESI)

Highly efficient and reversible iodine capture using a metalloporphyrin-based conjugated microporous polymer

Sigen A,^a Yuwei Zhang,^a Zhongping Li,^a Hong Xia,^c Ming Xue,^b Xiaoming Liu,^{*a} and Ying Mu^a

^a State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Avenue, Changchun, 130012, P.R.China.

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, P.R.China.

^c State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Technology, Jilin University, Changchun, 130012, P.R.China

Email: xm_liu@jlu.edu.cn

Section 1. Materials and Methods

The pyrrole, *p*-Bromobenzaldehyde, acetic acid, Ni(COD)₂ and activated carbon (BET = $600 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.95 \text{ cm}^3 \text{ g}^{-1}$) were obtained from Aldrich. Zeolite 13X (BET = $373 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.34 \text{ cm}^3 \text{ g}^{-1}$) was obtained from Tianjin Fuchen Chemical Reagent Factory. 2,2'-bipyridine, COD, nickel acetate tetrahydrate were obtained from TCI Chemicals. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

Synthesis of 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin

A mixture of p-bromobenzaldehyde (3.72 g, 20 mmol) in nitrobenzene (100 mL) and acetic acid (150 mL) was heated up to 120 °C and was added with freshly distilled pyrrole (1.4 mL, 20 mmol). The mixture was stirred at 120 °C for 1h and cooled to room temperature. The dark violet precipitate was collected by filtration and washed with methanol (50 mL × 3). The product was purified by recrystallization twice from CHCl₃/MeOH, to give 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin as violet crystal (1.38 g) in 30% yield. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) –2.87 (s, 2H, N–H), 7.91 (d, 8H, J = 8.2 Hz, Ar–H), 8.07 (d, 8H, J = 8.2 Hz, Ar–H), and 8.84 (s, 8H, pyrrole–H). MALDI-TOF MS: m/z 929.89, calcd. for C₄₄H₂₆Br₄N₄; found, [M + H]⁺ 929.47.

Synthesis of nickel (II) 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin

To a mixture of 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin (200 mg, 0.22 mmol), CHCl₃ (15 mL) and AcOH (15 mL) was added with Ni(OAc)₂•4H₂O (548 mg, 2.20 mmol). After stirred at 120 °C for 2 h, the precipitate was filtered and washed with MeOH (10 mL × 3). The product was isolated by column chromatography as a purple solid (185 mg, 85% yield). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.84 (dd, 16H, J = 8.28 Hz, Ar–H), 8.73 (s, 8H, pyrrole–H). MALDI-TOF MS: m/z 987.21, calcd. for C₄₄H₂₄Br₄N₄Ni; found, [M]⁺ 986.57. IR (KBr, v; cm⁻¹): 1551, 1482, 1351, 1174, 1074, 998, 712, and 481. UV-Vis (λ ; nm): 424, 534, 625, and 659.

Synthesis of NiP-CMP

1,5-Cyclooctadiene (48 mg, 0.44 mmol) was added to a DMF solution (6 mL) of bis(1,5-cyclooctadiene)nickel(0) (123 mg, 0.44 mmol) and 2,2'-bipyridyl (70 mg, 0.44 mmol) and the mixture was heated at 80 °C for 1 h. To the mixture was added with nickel (II) 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin (100 mg, 0.10 mmol) and the mixture was stirred at 80 °C for 72 h to give a deep purple suspension. After cooling to room temperature, the mixture was added with acetate acid (10 mL) and stirred at room temperature for 10 h. After filtration, the residue was washed with CHCl₃ (30 mL × 5), THF (30 mL × 5), and water (30 mL × 5), respectively, and dried in vacuum, to give NiP-CMP as a deep-red powder (66 mg, 99% yield). Elemental analysis (wt%) calcd. For { $C_{44}H_{24}N_4Ni$ }n: C 78.80, H 3.69, N 8.55; found: C 76.16, H 4.06, N 7.78. IR (KBr, v; cm⁻¹): 3026, 1598, 1491, 1351, 1197, 1074, 1002 (δ Ni–N), 803, and 711. UV-Vis (λ ; nm): 448, 538, and 624.

¹H spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were performed on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode using 9-nitroanthracene or dithranol as a matrix. Solid-state ¹³C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. All ¹³C CP MAS chemical shifts

are referenced to the resonances of adamantane ($C_{10}H_{16}$) standard ($\delta CH_2 = 38.5$). The infrared spectra were recorded from 400 to 4000 cm⁻¹ on a Nicolet FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. The sample was prepared by drop-casting a methanol suspension of NiP-CMP onto a copper grid. The Pd contents in polymer frameworks were determined by Perkin-Elmer ICP-OES Optima 3300DV spectroscopy. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer diffractometer by depositing powder on glass substrate, from $2\theta = 4.0^{\circ}$ to 60° with 0.02° increment at 25 °C. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer within the wavelength range 200-700 nm, using the same solvent in the analyzed solution as a blank. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min⁻¹ from 25 to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size distribution.

Section 2. TGA Profile



Figure S1. TGA curve of NiP-CMP under nitrogen.

(a) <u>SE 5.0KV X30,000 100nm WD 8.2mm</u> (b)

Section 3. The SEM and TEM Images

Figure S2. SEM (a) and TEM (b) images of NiP-CMP.

Section 4. Powder X-Ray Diffraction



Figure S3. Powder X-ray diffraction pattern of NiP-CMP.

Section 5. FT IR Spectra



Figure S4. The IR spectra of NiP-CMP (blue line) and its monomers (black line).

Section 6. Solid State ¹³C CP/MAS NMR Spectrum



Figure S5. Solid ¹³C CP/MAS NMR spectroscopy of NiP-CMP. Signals with * symbols are side peaks.

Section 7. UV-Vis Spectral Profiles



Figure S6. The absorption spectra of NiP-CMP (blue line) and its monomer (black line).

Section 8. FT IR Spectra



Figure S7. IR spectra of NiP-CMP, I₂@CMP and I₂.

Section 9. Porphyrin-Based Porous Materials

ampleBET ($m^2 g^{-1}$)		Ref		
Porphyrin-based metal-or	ganic frameworks			
S _P	1187	Appl. Mater. Interfaces 2013, 5, 7654.		
S _{Cu}	932	Appl. Mater. Interfaces 2013, 5, 7654.		
CHF-1	1620	Chem. Mater. 2014, 26, 1639.		
MIL-141(A)	500-860	Chem. Mater. 2011, 23, 4641.		
Cu ₂ (AcO) ₄ -(CuTPyP) _{1/2}	812	Inorg. Chem. 2006, 45, 7988.		
Zr-PCN-221	1936	Inorg. Chem. 2013, 52, 12661.		
Zr-PCN-221(Fe)	1549	Inorg. Chem. 2013, 52, 12661.		
Hf-PCN-221(Co)	1532	Inorg. Chem. 2013, 52, 12661.		
(G-dye-FeP) _n MOF	933	J. Am. Chem. Soc. 2012, 134, 67073.		
MMPF-8	440	CrystEngComm, 2013, 15, 9320.		
MOF-525	2620	Inorg. Chem. 2012, 51, 6443.		
MOF -545	2260	Inorg. Chem. 2012, 51, 6443.		
BOP-MOF	540	J. Am. Chem. Soc. 2011, 133, 15858.		
MMPF-5(Co)	600	Chem. Eur. J. 2013, 19, 3297.		
ZnMn-RPM	1000	J. Am. Chem. Soc. 2011, 133, 5652.		
Porphyrin-based porous o	rganic polymers			
ZnP-COF	1742	Chem. Commun., 2011, 47, 1979.		
COF-366	735	Chem. Mater., 2011, 23, 4094.		
COF-66	360	Chem. Mater., 2011, 23, 4094.		
CuP-SQ COF	539	Angew. Chem. Int. Ed. 2013, 52, 3770.		
DhaTph	1305	Angew. Chem. Int. Ed. 2013, 52, 13052.		
CuP-TFPh ₅₀ COF	1389	J. Am. Chem. Soc. 2013, 135, 546.		
CuPor-BPDC	442	Polym. Chem. 2013, 4, 4566.		
H ₂ P-COF	1126	Chem. Commun. 2014, 50, 1292.		
PPOP-2	950	J. Am. Chem. Soc. 2013, 135, 11720.		
POP-1~ POP-3	875~750	Chem. Commun. 2012, 48, 248.		
CoPc-PIM-B	450-600	J. Mater. Chem. 2008, 18, 573.		
FeP-CMP	1270	J. Am. Chem. Soc. 2010, 132, 9138.		
Fb-PPOP	355 ± 50	Chem. Sci. 2011, 2, 686.		
Ni-Por-1	1711	Macromolecules 2012, 45, 7413.		
(Zn,Cu,Co)P ₁ –CMP	1140,1247,1080	Chem. Commun. 2013, 49, 3233.		
ZnP ₂ –CMP	1130	Chem. Commun. 2013, 49, 3233.		
ZnP-CTF	1510	Polym. Chem. 2013, 4, 2445.		
Al-PPOP-1 and 2	640 and 660	J. Am. Chem. Soc. 2013, 135, 11720.		
FePorph-PIM	866	J. Mater. Chem. 2008, 18, 573.		
P(Fe-TTPP)	1248	Macromolecules 2010, 43, 3325.		

Table S1. Summary of surface area of porphyrin-based porous materials

Section 10. I₂ Uptake of Porous Materials

Sample	BET	Т	Iodine uptake	Ref
	$(m^2 g^{-1})$	(°C)	(wt.%)	
$[Zn(C_6H_8O_8)] \cdot 2 H_2O$	—	19	16.6	Angew. Chem. Int. Ed. 2003, 42, 1848.
$[Fe_3(HCOO)_6](I_2)_{0.84}$	385	25	32.8	Adv. Funct. Mater. 2007, 17, 1523.
$[Zn_3(DL-lac)_2(pybz)_2]3I_2$	763	25	49.7	J. Am. Chem. Soc. 2010, 132, 2561.
ZIF-8	1630	77	55.6	J. Am. Chem. Soc. 2011, 133, 12398.
CC3	624	20	35.8	J. Am. Chem. Soc. 2011, 133, 14920.
3D Cd(II)-triazole MOF	—	25	46	Chem. Commun. 2011, 47, 7185.
Mon-POF	1230	70	25	Chem. Mater. 2012, 24, 1937.
HKUST-1	1500-2100	75	63.6	Chem. Mater. 2013, 25, 2591.
Cu-BTC	—	75	175	Chem. Mater.2013, 25, 2591.
$\{[(CuI)_2(2)]\}_n$	—	25	52.4	Angew. Chem., Int. Ed. 2013, 52, 12395.
JUC-Z2	2081	60	80.4	J. Mater. Chem. A 2014, 2, 7179.
Polyurethane (PU1)		70	56.5	Polymer 2006, 47, 2728-2740.
TPP		80-100	26.4-29.3	Angew. Chem. Int. Ed. 2002, 41, 2281.
L-Leucyl-L-serine	_	25	3.8	Chem. Commun. 2005, 4288.
[Cu(IN)2] (IN: isonicotinato)	_	140	45.2	Chem. Commun. 2003, 1346.
$[Zn_7(L1)_3(H_2O)_7]_n \cdot [Zn_5(L1)_3(H_2O)_5]_n$ xsolvent	373	25	$1.2.65I_2$	Chem. Commun. 2011, 47, 6425.
${[Cu_6(pybz)_8(OH)_2] I_5 I_7}_n$	—	140	43.2	J. Am. Chem. Soc. 2012, 134, 4857.
$[Zn(C_6H_8O_8)] \cdot \approx 2 H_2O$	—	19	16.6	Angew. Chem. Int. Ed. 2003, 42, 1848.
$[WS_4Cu_4(4,4\text{`-bpy})_4][WS_4Cu_4I_4(4,4\text{'-bpy})_2]$	_	25	32.9	Angew. Chem. Int. Ed. 2004, 43, 4741.

Table S2. Summary of surface area and iodine sorption properties of porous materials

Section 11. XPS Spectra



Figure S8. XPS spectrum of NiP-CMP after iodine capture.

Section 12. Recycable Uptake for Iodine



Figure S9. Reusability of NiP-CMP for iodine adsorption by vapor sublimation.





Figure S11. Calibration plot of standard iodine by UV/vis spectra in cyclohexane solution (a) and ethanol solution (b), respectively. Inset: the fitting of Abs value vs concentration of I_2 with the relatively good linearity satisfies Lambert-Beer Law.



Figure S12. The selected UV/vis spectra of the filtrate collected at different time for the adsorption process of iodine in a cyclohexane solution of 2 mg mL⁻¹ (a) and 6 mg mL⁻¹ (b), respectively. The solution was diluted respectively to get appropriate absorption value.

Sorption Kinetics

Pseudo first order kinetic model

The linear form of pseudo first order kinetic model is expressed by the following equation: $\ln(Q_e - Q_t) = \ln Q_e - k_1 t$

Where Q_t and Q_e are the amount of iodine adsorbed at time t and equilibrium (mg/g),

 k_1 is the pseudo-first-order rate constant of adsorption process (h⁻¹).

The pseudo-second-order model

The linear form of pseudo first order kinetic model is expressed by the following equation: $\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$

Where Q_t and Q_e are the amount of iodine adsorbed at time *t* and equilibrium (mg/g), k_2 is the pseudo-first-order rate constant of adsorption process (g/mg h).



Figure S13. The pseudo-first-order model (red line) and the pseudo-second-order model (black line). (a) Initial concentration of iodine solution: 2 mg mL^{-1} . (b) Initial concentration of iodine solution: 6 mg mL^{-1} .

Table S3. Parameters of the different adsorption kinetic models extracted from

 experimental adsorption data for NiP-CMP.

Adsorbent	Pseu	do-first-ord	er	Pseudo-second-order		
	$k_1(1/h)$	Q _e (mg)	R^2	k_2 (g/(mg h)	Q _e (mg)	R^2
2 mg/ml	0.3435	2.93	0.9526	0.1554	3.21	0.9997
6 mg/ml	1.671	7.03	0.7182	0.4859	7.24	0.9262

Table S4.	Quantitative	results	of iodine	uptake	by 1	NiP-CMP,	activated	carbon	and
zeolite 13X	K in cyclohexa	ane solut	tion. ^a						

Sample	Time (h)	Iodone uptake (mg)
NiP-CMP	48	5.7
Activated carbon	48	2.1
Zeolite 13X	48	0.15

 a 85 mg of different adsorbents immersed in a 3 mL cyclohexane solution if iodine with a same concentration of 2 mg mL⁻¹

Adsorption isotherm models

The Langmuir isotherm model:

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e}$$

The Feundlich isotherm model:

$$Q_e = k_F C_e^{\frac{1}{n}}$$

Where k_L (l/mg) and Q_m (mg/g) are the Langmuir isotherm constants; k_F (l/mg) and n are the Feundlich isotherm constants; C_e are the concentration at equilibrium (mg/L), Q_e are the amount of iodine adsorbed at equilibrium (mg/g).



Figure S14. Adsorption isotherm of iodine (a) Langmuir line and (b) Freündlich line at room temperature.

Table S5. Parameters of the different isotherm models extracted from experimental adsorption isotherms data for NiP-CMP.

Langmuir isotherm			Freundlich isotherm		
Q _m (mg/g)	$k_{\rm L}({\rm l/mg})$	R^2	$k_{\rm F}$ (l/mg)	n	R^2
342	9.84	0.988	2.438	1.844	0.966

Section 14. Photography



Figure S15. The color change of the ethanol solution (1 mL) of I_2 @NiP-CMP (30 mg) with time.

Section 15. Release of Iodine



Figure S16. Temporal evolution of the I₂-release amount for I₂@NiP-CMP.

Section 16. Porosity of NiP-CMP after Five Times Reuse



Figure S17. Nitrogen sorption isotherm (a) and Pore size distribution (b) of NiP-CMP after 5 times reuse.