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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

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

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

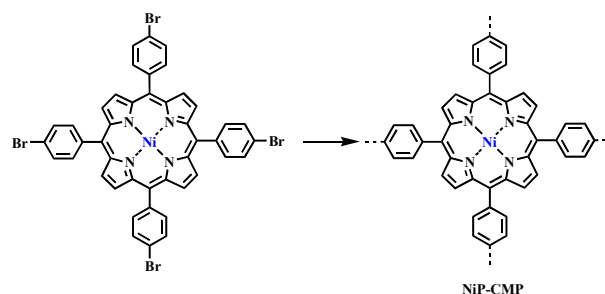
DOI: 10.1039/b000000x

A new metalloporphyrin-based conjugated microporous polymer, NiP-CMP, was constructed via homo-coupling polymerization reaction. NiP-CMP possesses high BET surface area of over 2600 m² g⁻¹, large pore volume of 2.288 cm³ g⁻¹ and as well as good stability, and display excellent guest uptake of 202 wt% in iodine vapour. We also highlight that the polymer exhibits outstanding performance in the reversible adsorption of iodine in solution.

The demand for clean and safe nuclear energy is growing in the worldwide to meet the necessary energy requirements for the future without the production of greenhouse gas emissions. A main issue of concern for safety associated with nuclear energy is appropriate nuclear waste management involved with health effects of radiation.¹ ¹²⁹I is an important radioisotope in nuclear waste, and has a particularly long-live (half-life of 1.57 × 10⁷ years) and has hence generated strong interest and concern. However, the leading approach to the efficient capture and reliable storage radioactive gaseous byproduct such as iodine in nuclear effluents remains challenging.² Currently, the inorganic solid adsorbents, such as silver-based zeolites were used to capture radioactive iodine.³ However, these silverloaded adsorbents have low adsorption capacities, owing to their limited available surface areas. Especially, main disadvantages for silver-based zeolites are related to high cost and the adverse environmental impact of silver metal. Crystalline metal-organic frameworks (MOFs) have recently been exploited as a new type of sorbents for capturing iodine, and they exhibited high uptake capacity.⁴ But the poor water and moisture stability of most MOFs casts a shadow on their practical application in storage of iodine, attributed to the off-gas of fuel reprocessing plants contains high levels of water vapor. In the context, therefore, the development of a new class of outstanding porous sorbents with high surface area, large pore volume, robust chemical and thermal stability for capturing iodine is also an important challenge.

Over the past several years, covalently linked porous organic polymers (POPs) including crystalline covalent organic frameworks,⁵ triazine-based organic frameworks,⁶ and amorphous hyper-crosslinked polymers,⁷ conjugated microporous polymers,⁸ polymers of intrinsic microporosity,⁹ element organic frameworks¹⁰ and porous aromatic frameworks¹¹ can be construct from well-functional organic building blocks and represent a newly fascinating class of nanoporous materials with excellent stability, and they have been demonstrated great potential application in energy related scopes. Metalloporphyrin complexes are excellent catalysts for many molecular transformations and important components for photoelectric materials. Generally, porous materials based on metalloporphyrin building blocks are

easily functionalized, and have excellent thermal stability, which is attributed to the hybrid properties of metalloporphyrin segments. Indeed, the recent research results demonstrated that the metalloporphyrin-based POPs are excellent heterogeneous catalysts,¹² gas adsorbents,¹³ high-rate charge carrier transporters.¹⁴ Up to now, however, the iodine adsorption and storage properties of covalently linked porous organic polymer frameworks have not been explored. With these considerations in mind, in this contribution, we report herein on the construction of a metalloporphyrin-based conjugated microporous polymer (NiP-CMP) utilizing Nickel (II) 5,10,15,20-tetrakis(4-bromophenyl)porphyrin as a building block by a bottom-up strategy. NiP-CMP possesses unique microporous character with high surface area, large pore volume, perfect chemical and thermal stability and high adsorption capacity for iodine vapour. As expected, the resulted polymer framework also exhibits an exceptional performance in the reversible adsorption of iodine.



Scheme 1. Synthetic route for NiP-CMP using Nickel (II) 5,10,15,20-tetrakis(4-bromophenyl)porphyrin as a building block.

NiP-CMP was prepared in high yield by the well-established Yamamoto homocoupling polycondensation reaction (Scheme 1).¹¹ The NiP-CMP is red-brown powder with a low density and insoluble in water or common organic solvents. It is chemically stable, even exposed to dilute solution of acid and base, suggesting highly cross-linked and robust structures. The NiP-CMP was characterized by infrared spectroscopy (IR), ¹³C cross polarization magic angle spinning (CP/MAS) NMR, thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The NiP-CMP is stable in nitrogen atmosphere and no mass loss is observed up to 300 °C by TGA (Fig. S1). It is gradually decomposed at elevated temperature, but it also retained the 85% of its initial mass at 700 °C. SEM images displayed that the polymer adopt a spherical shape with sizes of 50-100 nm (Fig. S2a). TEM revealed the homogeneous distribution of nanometer-

scale pores in the textures (Fig. S2b). PXRD profiles did not show any strong signals, indicating that NiP-CMP is an almost amorphous polymer (Fig. S3). The success of the phenyl-phenyl coupling was confirmed by FT-IR measurements. Compared with the monomer, the peak at 481 cm^{-1} for C-Br band vibration modes of starting material almost disappeared after polymerization. In addition, the bands at 3029 cm^{-1} , 1606 cm^{-1} and 1492 cm^{-1} are associated with the C-H stretch in phenyls, the C=C stretch in phenyls and C=C stretch in porphyrin, respectively. The peak at 1013 cm^{-1} can be ascribed to Ni-N stretch (Fig. S4). Furthermore, the structure of NiP-CMP was characterized at molecular level by solid state ^{13}C CP/MAS NMR (Fig. S5). In addition, elemental analysis confirmed that the weight percentages of C, H, and N contents were close to the theoretical values of its infinite 2D polymer. The electronic adsorption spectroscopy of NiP-CMP also retained peak features of metalloporphyrin building block and a broad Soret band appeared at 448 nm , which is red-shifted 24 nm from that of its monomer (Fig. S6).

In order to characterize the porosity parameters of NiP-CMP, the nitrogen sorption isotherms were measured at 77 K . As shown in Fig. 1a, the NiP-CMP exhibits a combination of type-I and II nitrogen sorption isotherm featured according to the IUPAC classification and show a steep nitrogen gas uptake at low relative pressure, thus reflecting the microporous nature of the network. The nitrogen sorption increases with increasing pressure, which indicates a large external surface area owing to the presence of small particles. In addition, a hysteresis can be observed at low relative pressures for NiP-CMP based on the isotherms, this phenomenon is associated with the irreversible uptake of gas molecules in the pores. It probably means a swelling in a flexible framework at 77 K by nitrogen.^{10a,15} Derived from the N_2 adsorption data, NiP-CMP has a BET specific surface area of $2630\text{ cm}^2\text{ g}^{-1}$. To the best of our knowledge, this surface area is the highest in metalloporphyrin-based organic porous materials that have been reported, and even competitive with the best reported metalloporphyrin-based MOFs (Table S1). The NiP-CMP has wide pore size distribution, with the pore widths centering around 0.70 , 0.85 , 0.95 and 1.25 nm , respectively, as calculated from Saito-Flory method (Fig. 1b). The total volume calculated with nitrogen gas adsorbed at $P/P_0 = 0.99$ was $2.288\text{ cm}^3\text{ g}^{-1}$.

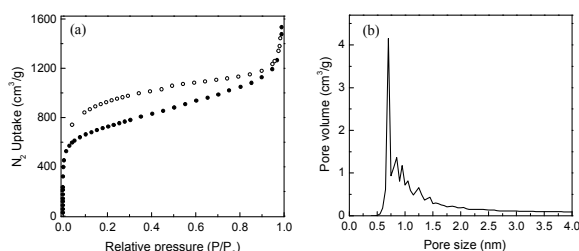


Fig. 1 Nitrogen adsorption/desorption isotherms (filled circles: adsorption, open circles: desorption) (a) and Pore size distribution (b) of NiP-CMP.

The NiP-CMP has excellent porous characters and remarkable stability, and these features prompted us to examine its adsorption properties for iodine. The samples of NiP-CMP powder were placed in a sealed vessel in the presence of solid iodine. The iodine sublimed into the porous adsorbent over time at 350 K and ambient pressure, which is a typical fuel reprocessing conditions. As time went to, the color of the samples changed from red-brown to almost black. Gravimetric measurements taken at various time intervals during the iodine uptake, and the results showed that the mass of NiP-CMP samples increased

significantly with prolonging contact time. The maximum adsorption capacity on NiP-CMP was reached relatively quickly. No more change in the iodine loading amount were observed after 24 h, indicating that the system was basically saturated (Fig. 2a). Pleasantly, the iodine loading of $202\text{ wt}\%$ is higher than previously reported values of iodine uptake for the porous adsorbents (Table S2).^{3,4,16} Compared with NiP-CMP, no significant spectroscopic shifts were observed for iodine-loaded polymer $\text{I}_2@$ NiP-CMP in Fourier transform infrared (Fig. S7). X-ray photoelectron spectroscopy (XPS) of $\text{I}_2@$ NiP-CMP indicated that the valence of the encapsulated iodine species is zero, which confirmed that the included iodine species exists as I_2 (Fig. S8). Thermogravimetric analysis (TGA) graph of $\text{I}_2@$ NiP-CMP displayed a broad mass loss step from 90 to $300\text{ }^\circ\text{C}$ (Fig. 2b), and the calculated iodine mass loss was $194\text{ wt}\%$, which is close to the saturated adsorption value. Pleasantly, the recovered polymer was washed with ethanol to remove the adsorption iodine, dried in vacuum, reused in the next round of adsorption. The NiP-CMP can be efficiently recycled and reused for five repeating without significant loss of the iodine uptake (Fig. S9).

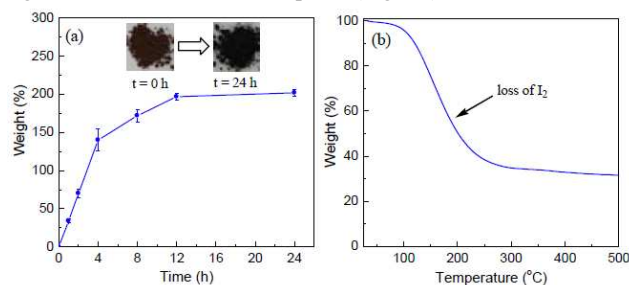


Fig. 2 (a) Gravimetric uptake of iodine as a function of time at 350 K . Inset: The photographs reveal the color change of the samples of NiP-CMP before and after iodine adsorption. (b) TGA trace of $\text{I}_2@$ NiP-CMP.

In addition, the NiP-CMP is capable of trapping iodine in solution. The adsorption kinetics of iodine at $25\text{ }^\circ\text{C}$ was presented in Fig. 3a. It can be seen that two stages of adsorption kinetics were obtained: the adsorption capacity of iodine increase quickly during the first 20 h and after that show increase were observed until equilibrium was reached. Removal efficiencies of 56 and 48% were achieved for iodine solutions of 2 and 6 mg mL^{-1} , respectively, which compared with that of functionalized MIL-53- NH_2 .¹⁷ The adsorption over NiP-CMP was analyzed using Lagergren pseudo-first-order and pseudo-second-order kinetic models.¹⁸ For the pseudo-second-order kinetic models, good linear fits with correlation coefficient R^2 values of above 0.999 and 0.926 were achieved for iodine solution of 2 and 6 mg mL^{-1} (Table S3). This suggested that the present adsorption system can be represented by the pseudo-second-order kinetic models in the adsorption data. Indeed, then the samples of polymer were immersed in a cyclohexane solution of iodine at $25\text{ }^\circ\text{C}$, the color of polymer gradually changed from red-brown to dark brown. Moreover, the color of the solution of iodine in cyclohexane turned paler.

The adsorption isotherm is a significant factor in determining the saturate adsorption capacity when the equilibrium is attained. As shown in Fig. 3b, the adsorption plot of equilibrium concentration versus adsorption capacity indicated two processes. One, the adsorption was a function of the initial concentration. Next, the adsorption reached the maximum adsorption uptake, becoming a concentration-independent process. From the kinetic studies, NiP-CMP presents the high sorption capacity with an iodine uptake of 326 mg g^{-1} . Indeed, the same weights (85 mg) different adsorbents immersed in a 3 mL cyclohexane solution of iodine with a same concentration of 2 mg mL^{-1} . Fig 3c displays

that the uptake of iodine on NiP-CMP is remarkable and clearly exceeds that of activated carbon and zeolite 13X in the cyclohexane solution of iodine, and quantitative results for iodine adsorption are given in Table S4. The highly uptake capacity of NiP-CMP for iodine may be attributed to excellent porosity, besides the conjugated π -electron framework may produce a weak interact with iodine, thereby increasing the adsorption amount for iodine.^{4d,f} In addition, the different models have been considered for the sorption isotherm curve (Fig. S14 and Table S5). The Langmuir equation fit well the sorption curve, suggesting a monolayer adsorption of iodine on the polymer surface.

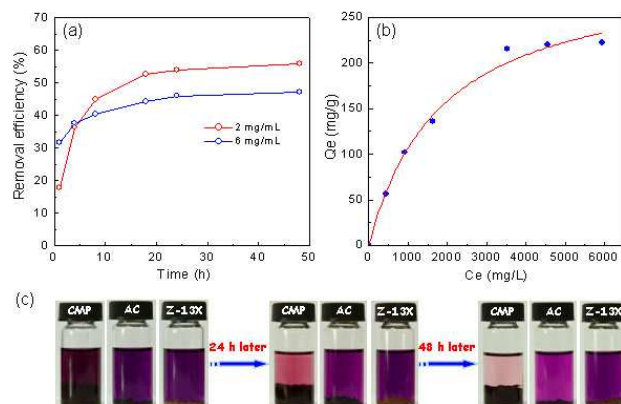


Fig. 3 (a) Kinetic studies of iodine adsorption by NiP-CMP in cyclohexane solutions. (b) Adsorption isotherm of iodine onto NiP-CMP. 30 mg NiP-CMP was stirred in 3 mL of solutions for 48 h. Straight line: Langmuir. (c) The photographs display the different inclusion rates and degrees of zeolite 13X, activated carbon and NiP-CMP.

Notably, this iodine sorption of NiP-CMP is reversible. The encapsulated iodine could be easily removed from the framework upon immersion of $I_2@NiP-CMP$ in organic solvents. Then the iodine-loaded samples of NiP-CMP were soaked in fresh ethanol, the color of the polymer changed gradually from dark to red-brown and, correspondingly, the color of the ethanol solution deepened from colorless to purple, which clearly indicates that the guests are dissociated from the NiP-CMP framework (Fig. S15). To investigate the kinetics of iodine delivery of NiP-CMP, the UV/Vis spectra were recorded at 25 °C. The absorbance of iodine in ethanol increased linearly with treatment time (Fig. S16). Typically, 15 mg of the $I_2@NiP-CMP$ samples were soaked in 1 mL ethanol. The iodine-release rate becomes slower after 2 h owing to the concentration of iodine in ethanol increased with time. After 8 h, however, about 96% of the initial iodine had been released from $I_2@NiP-CMP$, indicating the reversibility of the iodine adsorption process. In addition, NiP-CMP after five times reuse remains also a high surface area and large pore volume of over $2100\text{ cm}^2\text{ g}^{-1}$ and $2.0\text{ cm}^3\text{ g}^{-1}$ (Fig. S17), which attributed to its strongly skeletal structure.

In summary, a metalloporphyrin-based porous organic polymer framework NiP-CMP was successfully designed and synthesized by a bottom-up strategy. The new polymer has an excellent porosity with a high BET surface area of over $2600\text{ m}^2\text{ g}^{-1}$, a large pore volume and displays the highest reported value of iodine uptake for the porous adsorbents to date. The absorbed iodine could be recovered, and the NiP-CMP sorbent was easily recycled for reuse. In addition, we also highlight that the new polymer exhibits excellent performance in the reversible adsorption of iodine in solution. Currently, the design and construction of new functional POPs for energy, environment and catalytic-related applications is underway in our laboratory.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 51203058, 51173061 and 21074043). X. Liu is also grateful for support by the Frontiers of Science and Interdisciplinary Innovation Project of Jilin University (No. 450060481015).

Notes and references

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- † Electronic Supplementary Information (ESI) available: Synthesis of monomer and polymer, FT-IR, PXRD, TGA, UV-Vis, SEM, TEM and ^{13}C CP/MAS NMR of NiP-CMP and sorption kinetics. See DOI: 10.1039/b000000x/
- R. C. Ewing, F. N. von Hippel, *Science* 2009, **325**, 151.
- (a) D. R. Haefner and T. J. Tranter, Methods of Gas Phase Capture of Iodine from Fuel Reprocessing Off-Gas: A Literature Survey; INL/EXT-07-12299; Idaho National Laboratory: Idaho Falls, Idaho 83415, 2007; (b) B. J. Riley, J. Chun, J. V. Ryan, J. Matyas, X. S. Li, D. W. Matson, S. K. Sundaram, D. M. Strachan and J. D. Vienna, *RSC Adv.*, 2011, **1**, 1704.
- K. W. Chapman, P. J. Chupas, T.M. Nenoff, *J. Am. Chem. Soc.*, 2010, **132**, 8897.
- (a) D. F. Sava, K. W. Chapman, M. A. Rodriguez, J. A. Greathouse, P. S. Crozier, H. Y. Zhao, P. J. Chupas and T. M. Nenoff, *Chem. Mater.*, 2013, **25**, 2591; (b) D. F. Sava, M. A. Rodriguez, K. W. Chapman, P. J. Chupas, J. A. Greathouse, P. S. Crozier and T. M. Nenoff, *J. Am. Chem. Soc.*, 2011, **133**, 12398; (c) K. W. Chapman, D. F. Sava, G. J. Halder, P. J. Chupas and T. M. Nenoff, *J. Am. Chem. Soc.*, 2011, **133**, 18583; (d) M. H. Zeng, Q. X. Wang, Y. X. Tan, S. Hu, H. X. Zhao, L. S. Long, and M. Kurmoo, *J. Am. Chem. Soc.*, 2010, **132**, 2561; (e) Z. Yin, Q. X. Wang and M. H. Zeng, *J. Am. Chem. Soc.*, 2012, **134**, 4857; (f) Q. K. Liu, J. P. Ma and Y. B. Dong, *Chem. Commun.*, 2011, **47**, 7185; (g) Y. C. He, J. Yang, G. C. Yang, W. Q. Kan, J. F. Ma, *Chem. Commun.*, 2012, **48**, 7859.
- X. Feng, X. S. Ding and D. L. Jang, *Chem. Soc. Rev.*, 2012, **41**, 6010.
- P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450.
- J. Y. Lee, C. D. Wood, D. Bradshaw, M. J. Rosseinsky and A. I. Cooper, *Chem. Comm.*, 2006, 2670.
- (a) A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291; (b) X. Liu, Y. Xu and D. Jiang, *J. Am. Chem. Soc.*, 2012, **134**, 8738; (c) Y. H. Xu, S. B. Jin, H. Xu, A. Nagai and D. L. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012.
- N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675.
- (a) M. Rose, W. Böhlmann, M. Sabo and S. Kaskel, *Chem. Commun.*, 2008, 2462; (b) X. M. Liu, Y. W. Zhang, H. Li, S. G. A. H. Xia and Y. Mu, *RSC Adv.*, 2013, **3**, 21267.
- T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.* 2009, **48**, 9457.
- L. Chen, Y. Yang and D. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 9138.
- (a) X. M. Liu, H. Li, Y. W. Zhang, B. Xu, S. G. A. H. Xia and Y. Mu, *Polym. Chem.*, 2013, **4**, 2445; (b) X. M. Liu, Y. H. Xu, Z. Q. Guo, A. Nagai and D. Jiang, *Chem. Commun.*, 2013, **49**, 3233; (c) X. M. Liu, S. G. A. Y. W. Zhang, X. L. Luo, H. Xia, H. Li and Y. Mu, *RSC Adv.*, 2014, **4**, 6447.
- X. Feng, L. L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irie, Y. P. Dong, A. Nagai and D. L. Jiang, *Angew. Chem., Int. Ed.* 2012, **51**, 2618.
- (a) N. B. McKeown, P. M. Budd, K. J. Msayib, B. S. Ghanem, H. J. Kingston, C. E. Tattershall, S. Makhseed, K. J. Reynolds, D. Fritsch, *Chem. Eur. J.* 2005, **11**, 2610; (b) U. Stoeckl, G. Nickerl, U. Burkhardt, I. Senkovska, S. Kaskel, *J. Am. Chem. Soc.*, 2012, **134**, 17335.
- (a) P. S. Huang, C. H. Kuo, C. C. Hsieh and Y. C. Horng, *Chem. Commun.*, 2012, **48**, 3227; (b) T. Hasell, M. Schmidtman and A. I.

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- Cooper, *J. Am. Chem. Soc.*, 2011, **133**, 14920; (c) L. Dobrzanska, G. O. Lloyd, H. G. Raubenheimer and L. J. Barbour, *J. Am. Chem. Soc.*, 2006, **128**, 698;
- 17 C. Falaise, C. Volkringer, J. Facqueur, T. Bousquer, L. Gasnot and T. Loiseau, *Chem. Comm.*, 2013, **49**, 10320.
- 5 18 V. Vecaputhiran and G. Alagumuthu, *Int. J. Res. Chem. Environ.*, 2011, **1**, 42.

A robust metalloporphyrin-based conjugated microporous polymer has shown a high efficiency for iodine capture and reversible characters.

