Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Conjugated microporous polymers with the azide groups: A new strategy for postsynthetic fluorine functionalization en route for enhanced CO_2 adsorption properties

Di Cui,[a] Chan Yao[a] and Yanhong Xu*[a,b]

Corresponding Author:

Professor Yanhong Xu

[a]*Key Laboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Changchun, 130103, China*

[b]*Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Siping 136000, China*

Email: xuyh@jlnu.edu.cn

Contents

Section A. Materials and methods

Organic solvents for reaction were distilled over appropriate drying reagents under argon or obtained as dehydrated reagents from Kanto Chemicals. Deuterated solvents for NMR measurement were obtained from Cambridge Isotope Laboratories, Inc. Pyrrole, *p*-bromobenzaldehyde, acetic acid, nitrobenzene, 1,4-benzenediboronic acid, 4,4'-biphenyldiboronic acid, and $Pd(PPh_3)_4$ were obtained from Aldrich. 1,4-Dibromo-2,5-dimethylbenzene, tert-butyllithium, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and sodium azide were obtained from TCI. N-bromosuccinimide, dibenzyl peroxide, and zinc acetate hydrate were obtained from Kanto Chemicals. Concentrated HCl, methanol, tetrahydrofunan (THF), and acetone were purchased from Wako Chemicals. Chloroform and Calcium hydride were purchased from Kanto Co.

Fourier transform infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. UV-Vis-IR diffuse reflectance spectra (Kubelka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. The sample was prepared by drop-casting a THF suspension of the CMP samples onto a copper grid. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at a rate of 5 °C min^{-1} under a nitrogen atmosphere.

Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 120 °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 and pore size distribution.

Carbon dioxdie sorption isotherms were measured at 298 K and 273K with a Bel Japan Inc. model BELSORP-mini II analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Section B. Synthetic procedures

Synthesis of 5, 10, 15, 20-tetrakis(4’-bromophenyl)porphyrin[S1]

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 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). After isolated by column chromatography, the product was purified by recrystallization twice from $CHCl_3$/MeOH, to give 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin as a violet crystal (1.38 g) in 30% yield. ^{1}H NMR ($CDCl_3$, 400 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 $C_{44}H_{26}Br_4N_4$; found, $[M + H]^+$ 929.47.

Synthesis of zinc (II) 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin (ZnP)[S1]

To a mixture of 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin (360 mg, 0.39 mmol), $CHCl_3$ (20 mL) and AcOH (20 mL) was added $Zn(OAc)_2{\bullet}2H_2O$ (848 mg, 3.86 mmol). After stirred at 120 °C for 1.5 h, the precipitate was filtered and washed with MeOH (10 mL × 3). After isolated by column chromatography, the product was obtained as a purple solid (348 mg) in 90% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (d, 8H, J = 8.33 Hz, Ar–H), 8.07 (d, 8H, J = 8.33 Hz, Ar–H), 8.94 (s, 8H, pyrrole–H). MALDI-TOF MS: *m*/*z* 993.80, calcd. for $C_{44}H_{24}Br_4N_4Zn$; found, $[M]^+$ 992.71. IR (KBr; cm^{-1}): 1519, 1471, 1390, 1334, 1205, 1175, 1070, 1002, 797, 1070, 721, and 465. UV-Vis (λ; nm): 430, 592, and 624.

Synthesis of 2,2'-(2,5-dimethyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[S2]

1,4-dibromo-2,5-dimethylbenzene(5.28g, 20 mmol) was dissolved in dry THF (120 mL) and cooled to -80 °C. To the solution was added with tert-butyllithium (1.7 M) (40 mL, 68 mmol) very slowly under nitrogen. The mixture was stirred at – 40 °C for 3 h, cooled to – 80 °C again, and then was added with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mL, 49.2 mmol). The mixture was stirred at room temperature overnight, extracted with ethyl ether (150 mL), dried over anhydrous $MgSO_4$, and evaporated to dryness. The solid product was dissolved in boiling hexane and recrystallized at room temperature, to give white needle crystal in 42% yield (3.02 g, 8.43 mmol). ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.34 (s, 24H, $-CH_3$ × 8), 2.48 (s, 6H, $-CH_3$ × 6), 7.54 (s, 2H, $-C_6H_2-$).

Synthesis of 2,2-(2,5-bis(bromomethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[S2]

2,2'-(2,5-dimethyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1.20 g, 3.35 mmol) and N-bromosuccinimide (1.31 g, 7.37 mmol) were dissolved in benzene (20 mL). After nitrogen bubbling for 30 min, dibenzyl peroxide (10 mol%, 81.2 mg, 0.34 mmol) was added to the solution and the mixture was refluxed for 12 h. After cooling to room temperature, the solvent was evaporated. The residue was washed with methanol (100 mL) to give white solid in 82% yield (1.42 g, 2.75 mmol). ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.38 (s, 24H, $-CH_3 \times 8$), 4.88 (s, 4H, $-C_6H_2-CH_2-Br \times 2$), 7.79 (s, 2H, $-C_6H_2-$).

Synthesis of 2,2-(2,5-bis(azidomethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (N_3-BPB)[S2]

Sodium azide (0.63 g, 9.69 mmol) was added to a solution of 2,2'-(2,5-bis(bromomethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2.0 g, 3.88 mmol) in anhydrous THF (10 mL) and DMF (20 mL). The mixture was stirring at room temperature for 12 h, diluted with water (200 mL), extracted with ethyl acetate (100 mL). The combined organic layer was washed with water and dried over anhydrous MgSO4. The solvent was evaporated to give white solid in 82% yield (1.40 g, 3.18 mmol). ^{1}H NMR ($CDCl_3$) δ (ppm) = 1.36 (s, 24H, $-CH_3 \times 8$), 4.65 (s, 4H, $-C_6H_2-CH_2-N_3 \times 2$), 7.80 (s, 2H, $-C_6H_2-$).

Synthesis of ZnP-5%N_3-CMPs, ZnP-25%N_3-CMPs, ZnP-50%N_3-CMPs, ZnP-75%N_3-CMPs, and ZnP-100%N_3-CMPs

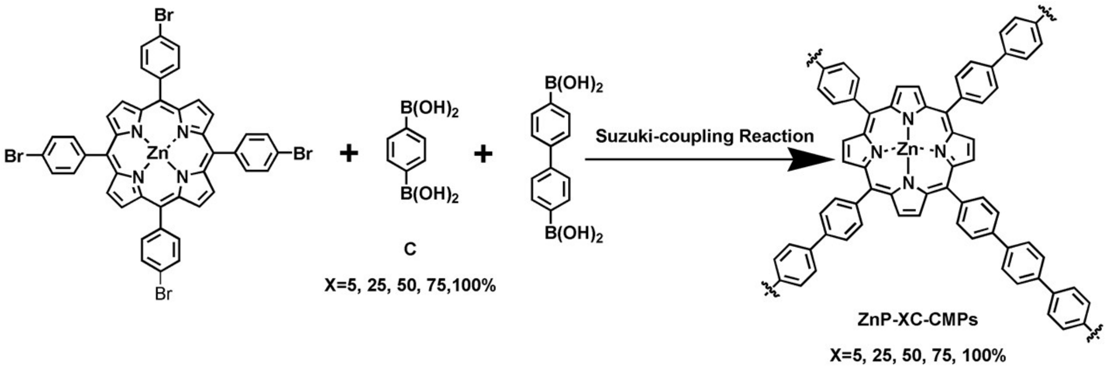
A mixture of ZnP (100 mg, 0.1 mmol), **N_3-BPB** (2.8 mg, 0.01 mmol for **ZnP-5%N_3-CMPs**; 14 mg, 0.05 mmol for **ZnP-25%N_3-CMPs**; 28 mg, 0.1 mmol for **ZnP-50%N_3-CMPs**; 42 mg, 0.15 mmol for **ZnP-75%N_3-CMPs**; 56 mg, 0.2 mmol for **ZnP-100%N_3-CMPs**; respectively), and 4,4'-biphenyldiboronic acid (46.2 mg, 0.19 mmol for **ZnP-5%N_3-CMPs**; 36.3 mg, 0.15 mmol for **ZnP-25%N_3-CMPs**; 24.2 mg, 0.1 mmol for **ZnP-50%N_3-CMPs**; 12.1 mg, 0.05 mmol for **ZnP-75%N_3-CMPs**; 0 mg, 0 mmol for **ZnP-100%N_3-CMPs**; respectively) in 1,4-dioxane (20 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 1.0 mL) and $Pd(PPh_3)_4$ (11.56 mg, 0.1 μmol). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 120 °C for 3 days. The precipitate was collected by filtration, thoroughly washed with water, dichloromethane, methanol, and tetrahydrofuran, dried under vacuum at 120 °C, and rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol, and THF, respectively, to give **ZnP-5%N_3-CMPs**, **ZnP-25%N_3-CMPs**, **ZnP-50%N_3-CMPs**, **ZnP-75%N_3-CMPs**, and **ZnP-100%N_3-CMPs** respectively, as gray powders in 81-97% isolation yields. Elemental analysis (%) C 77.22, H 4.39, N 4.82 (**ZnP-5%N_3-CMPs**); C 73.53, H 4.16, N 5.79 (**ZnP-25%N_3-CMPs**); C 68.74, H 4.13, N

7.53 (**ZnP-50%N_3-CMPs**); C 70.14, H 4.13, N 10.36 (**ZnP-75%N_3-CMPs**); and C 66.75, H 3.99, N 11.69 (**ZnP-100%N_3-CMPs**).

Synthesis of ZnP-5% F -CMPs, ZnP-25% F -CMPs, ZnP-50% F -CMPs, ZnP-75% F -CMPs, and ZnP-100% F -CMPs

(1) Synthesis of ZnP-5%F-CMPs: ZnP-5%N_3-CMPs (20 mg), CuI (2 mg), DMF (2 mL), DBu (300 μL), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (20 μL) were put into a 10 mL prex tube.

(2) Synthesis of ZnP-25%F-CMPs: ZnP-50%N_3-CMPs (20 mg), CuI (4 mg), DMF (2 mL), DBu (300 μL), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (40 μL) were put into a 10 mL prex tube.
(3) Synthesis of ZnP-50%F-CMPs: ZnP-50%N_3-CMPs (20 mg), CuI (8 mg), DMF (2 mL), DBu (300 μL), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (80 μL) were put into a 10 mL prex tube.
(4) Synthesis of ZnP-75%F-CMPs: ZnP-75%N_3-CMPs (20 mg), CuI (8 mg), DMF (2 mL), DBu (300 μL), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (120 μL) were put into a 10 mL prex tube.
(5) Synthesis of ZnP-100%F-CMPs: ZnP-100%N_3-CMPs (20 mg), CuI (8 mg), DMF (2 mL), DBu (300 μL), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (200 μL) were put into a 10 mL prex tube. The mixture was degassed by three freeze–pump–thaw cycles, then sealed by gun, heated at 50 °C for 3 days. The precipitate was collected by filtration, then KI solution (3.5 M, 3 mL) was added, stirred for 3h at R.T., filtered, thoroughly washed with water and tetrahydrofuran, dried under vacuum at 120 °C. Elemental analysis (%) C 77.22, H 4.39, N 4.82 (**ZnP-5%F-CMPs**); C 73.53, H 4.16, N 5.79 (**ZnP-25%F-CMPs**); C 68.74, H 4.13, N 7.53 (**ZnP-50%F-CMPs**); C 66.13, H 3.88, N 8.14 (**ZnP-75%F-CMPs**); C 63.25, H 3.73, N 8.22 (**ZnP-100%F-CMPs**).



Scheme S1. Schematic representation of synthesis of ZnP-XC-CMPs (X = 5, 25, 50, 75, 100) (C=benzene-1,4-diboronic acid).

Synthesis of ZnP-5%C-CMPs, ZnP-25%C-CMPs, ZnP-50%C-CMPs, ZnP-75%C-CMPs, and ZnP-100%C-CMPs

A mixture of ZnP (100 mg, 0.1 mmol), benzene-1,4-diboronic acid (C) (1.66 mg, 0.01 mmol for **ZnP-5%C-CMPs**; 8.3 mg, 0.05 mmol for **ZnP-25%C-CMPs**; 16.6 mg, 0.1 mmol for **ZnP-50%C-CMPs**; 24.9 mg, 0.15 mmol for **ZnP-75%C-CMPs**; 33.2 mg, 0.2 mmol for **ZnP-100%C-CMPs**; respectively), and 4,4'-biphenyldiboronic acid (46.2 mg, 0.19 mmol for **ZnP-5%C-CMPs**; 36.3 mg, 0.15 mmol for **ZnP-25%C-CMPs**; 24.2 mg, 0.1 mmol for **ZnP-50%C-CMPs**; 12.1 mg, 0.05 mmol for **ZnP-75%C-CMPs**; 0 mg, 0 mmol for **ZnP-100%C-CMPs**; respectively) in 1,4-dioxane (20 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 1.0 mL) and $Pd(PPh_3)_4$ (11.56 mg, 0.1 μmol). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 120 °C for 3 days. The precipitate was collected by filtration, thoroughly washed with water, dichloromethane, methanol, and tetrahydrofuran, dried under vacuum at 120 °C, and rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol, and THF, respectively, to give ZnP-5%C-CMPs, ZnP-25%C-CMPs, ZnP-50%C-CMPs, ZnP-75%C-CMPs, and ZnP-100%C-CMPs respectively, as gray powders in 84-96% isolation yields. Elemental analysis (%) C 82.32, H 4.18, N 3.22 (ZnP-5%C-CMPs), C 82.68, H 4.25, N 3.31 (ZnP-25%C-CMPs), C 83.02, H 4.23, N 3.15 (ZnP-50%C-CMPs), C 83.36, H 4.08, N 3.29 (ZnP-75%C-CMPs), and C 83.53, H 4.38, N 3.28 (ZnP-100%C-CMPs).

Section C. FT-IR spectra

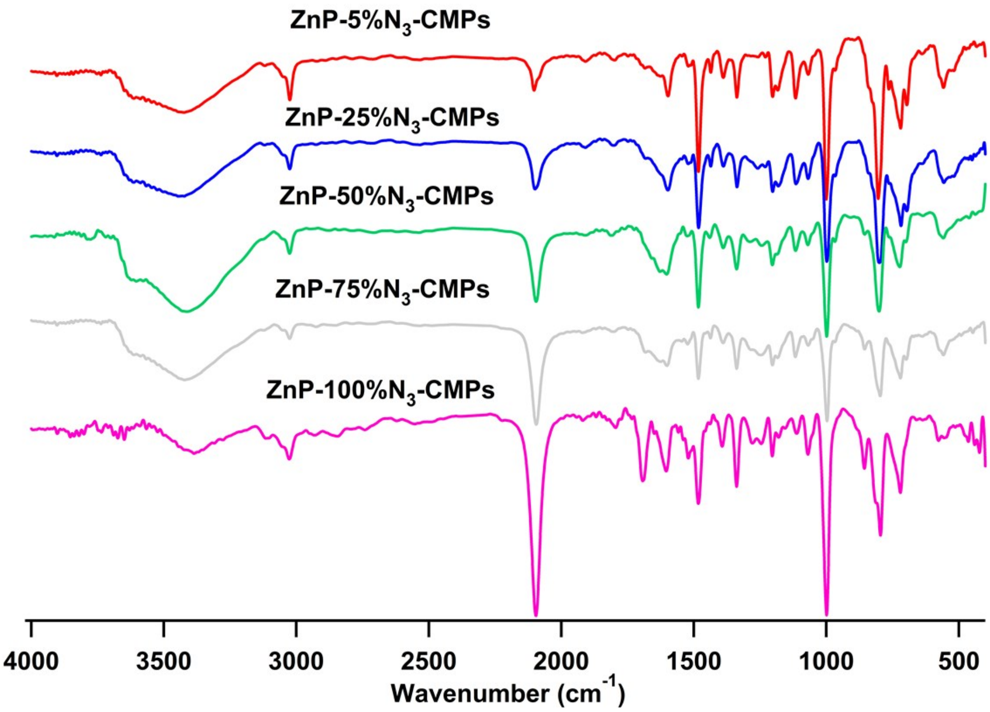


Fig. S1 FT-IR spectra of ZnP-XN$_3$-CMPs (X= 5, 25, 50, 75, and 100%).

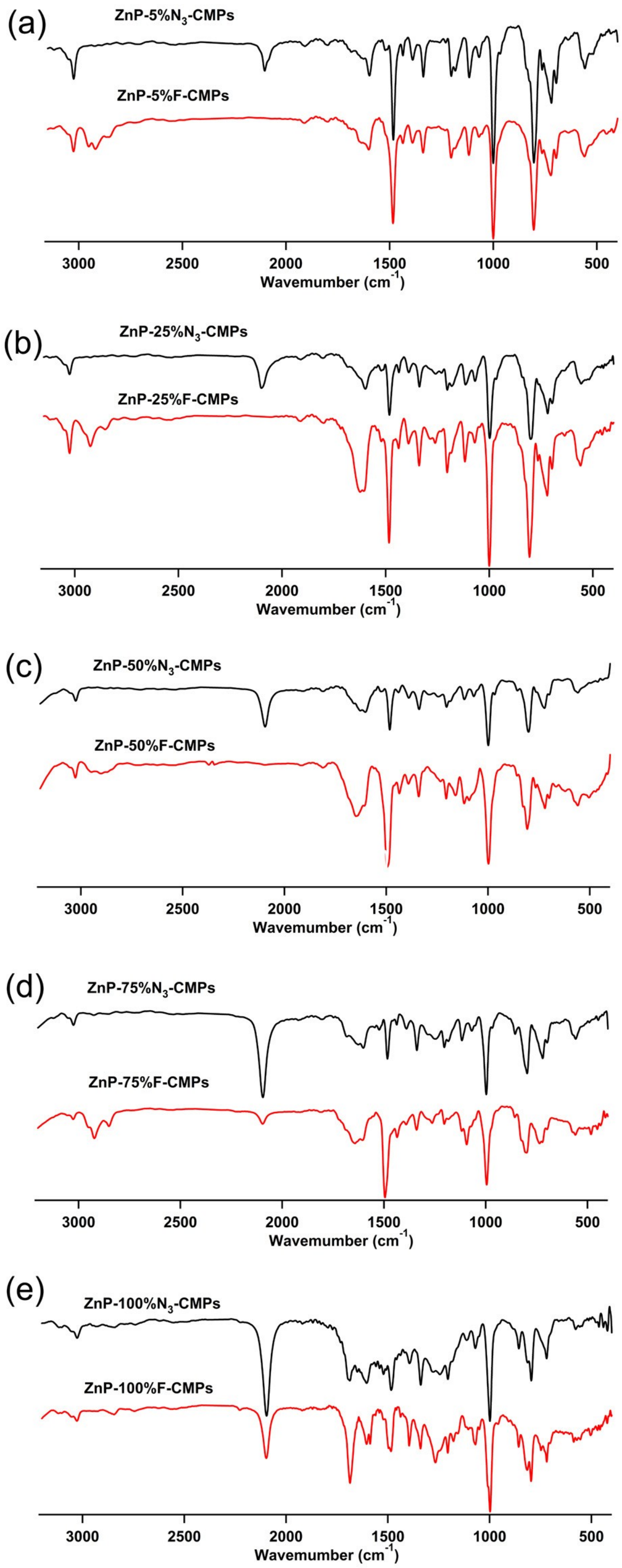


Fig. S2 FT-IR spectra of ZnP-XN_3-CMPs (X= 5, 25, 50, 75, and 100%) and ZnP-XF-CMPs (X= 5, 25, 50, 75, and 100%).

Section D. HR-TEM images

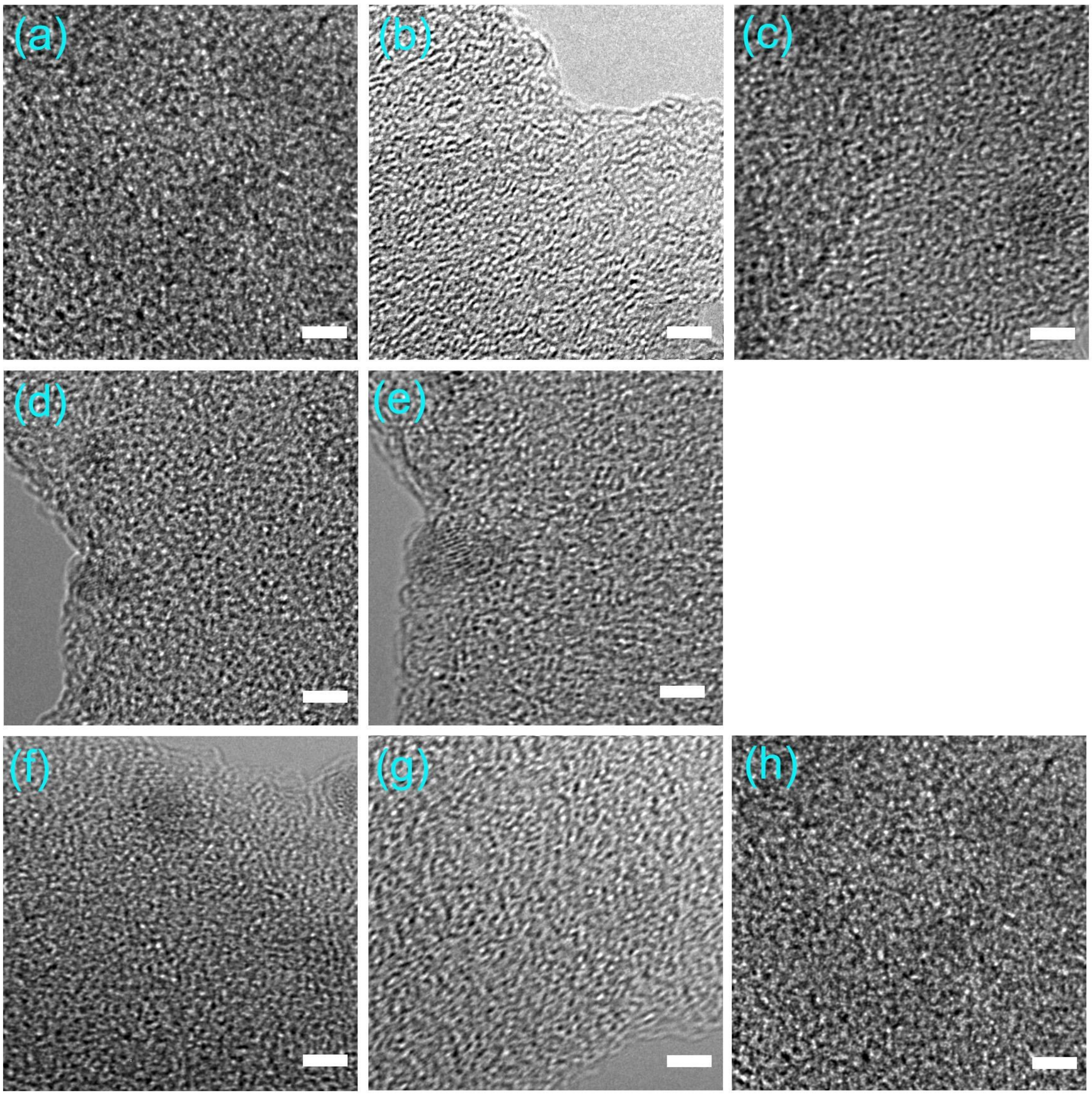


Fig. S3 HR-TEM images of (a) ZnP-5%N_3-CMPs, (b) ZnP-25%N_3-CMPs, (c) ZnP-50%N_3-CMPs, (d) ZnP-75%N_3-CMPs, (e) ZnP-100%N_3-CMPs, (f) .ZnP-5%F-CMPs, (g) ZnP-25%N_3-CMPs, and (h) ZnP-50%N_3-CMPs, respectively (Scale bar is 2 nm).

Section E. Powder X-ray diffraction patterns

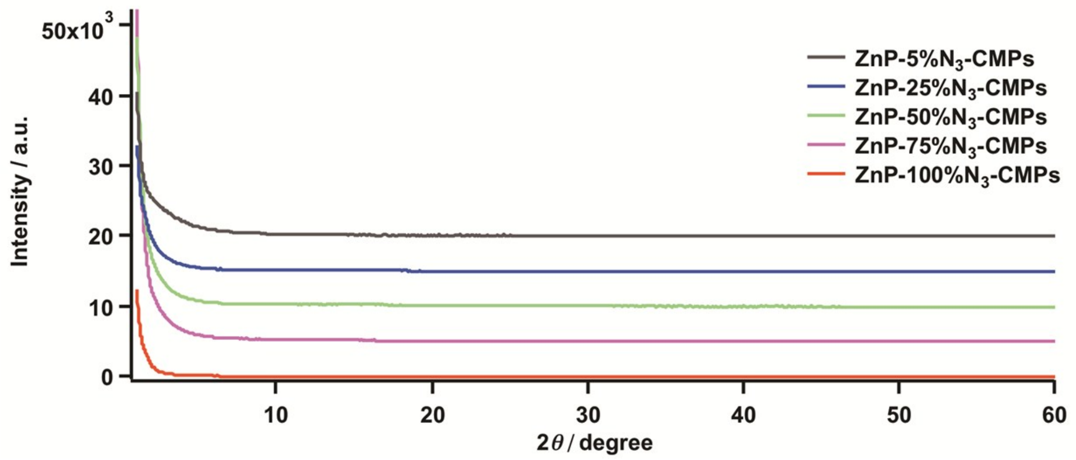


Fig. S4 PXRD spectra of ZnP-XN_3-CMPs (X= 5, 25, 50, 75, and 100%).

Section F. TGA curves

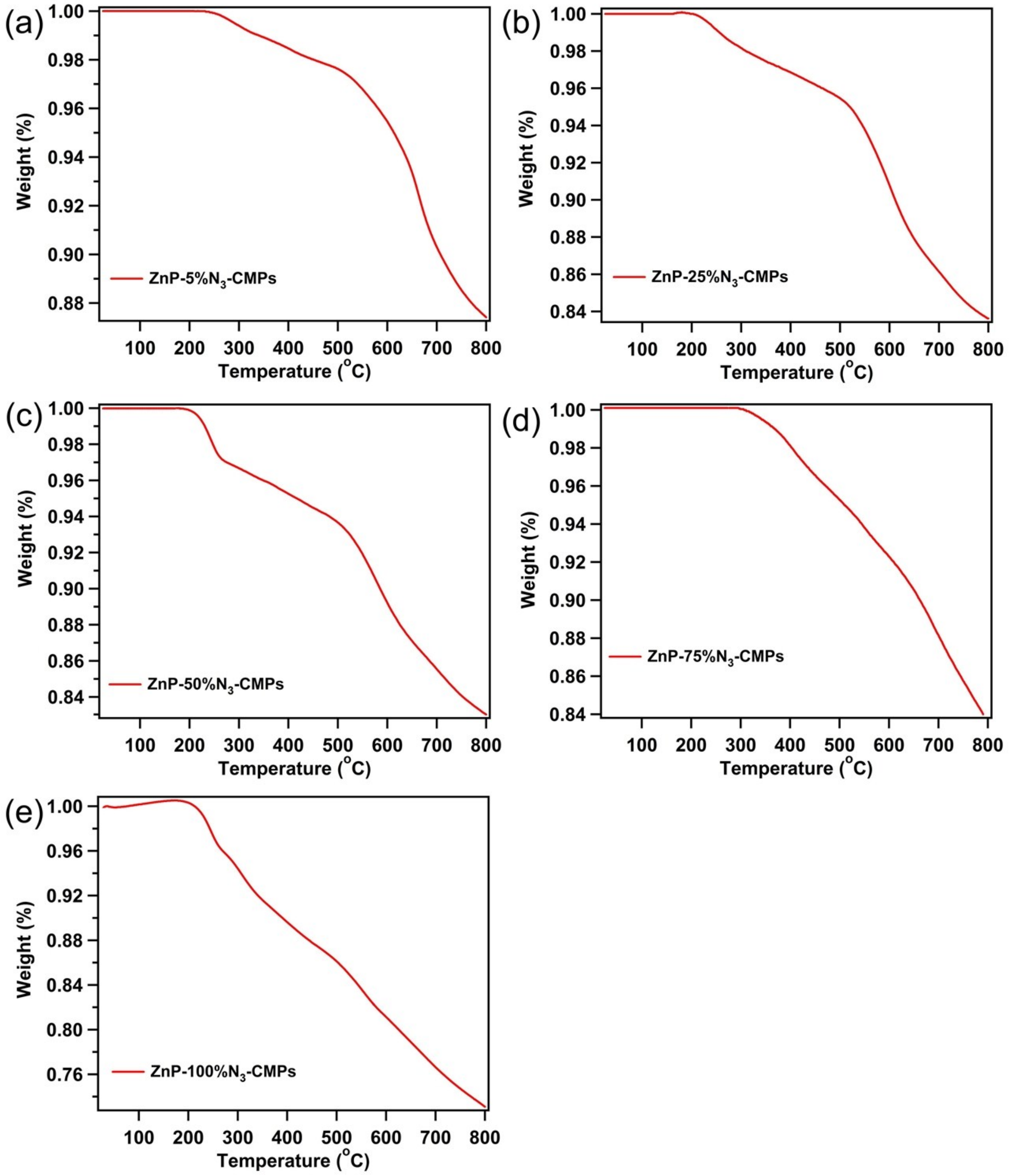


Fig. S5 TGA curves of ZnP-XN$_3$-CMPs (X= 5, 25, 50, 75, and 100%).

Section G. F1s XPS spectra

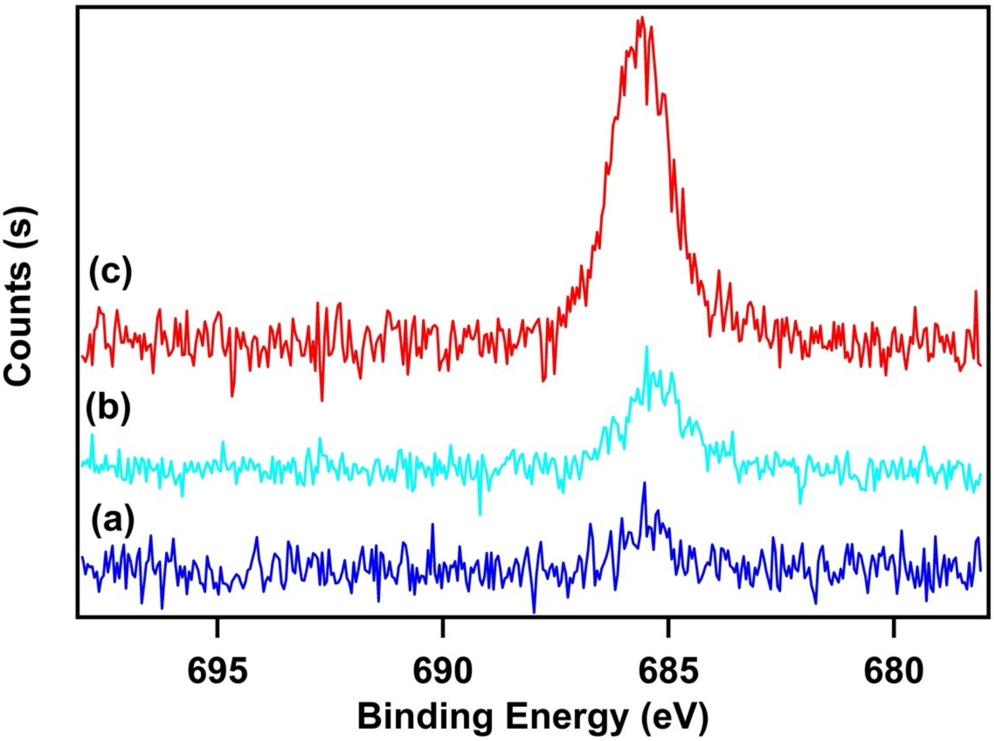


Fig. S6 F1s XPS spectra of (a) ZnP-5%F-CMPs, (b) ZnP-25%F-CMPs, and (c) ZnP-50%F-CMPs, respectively.

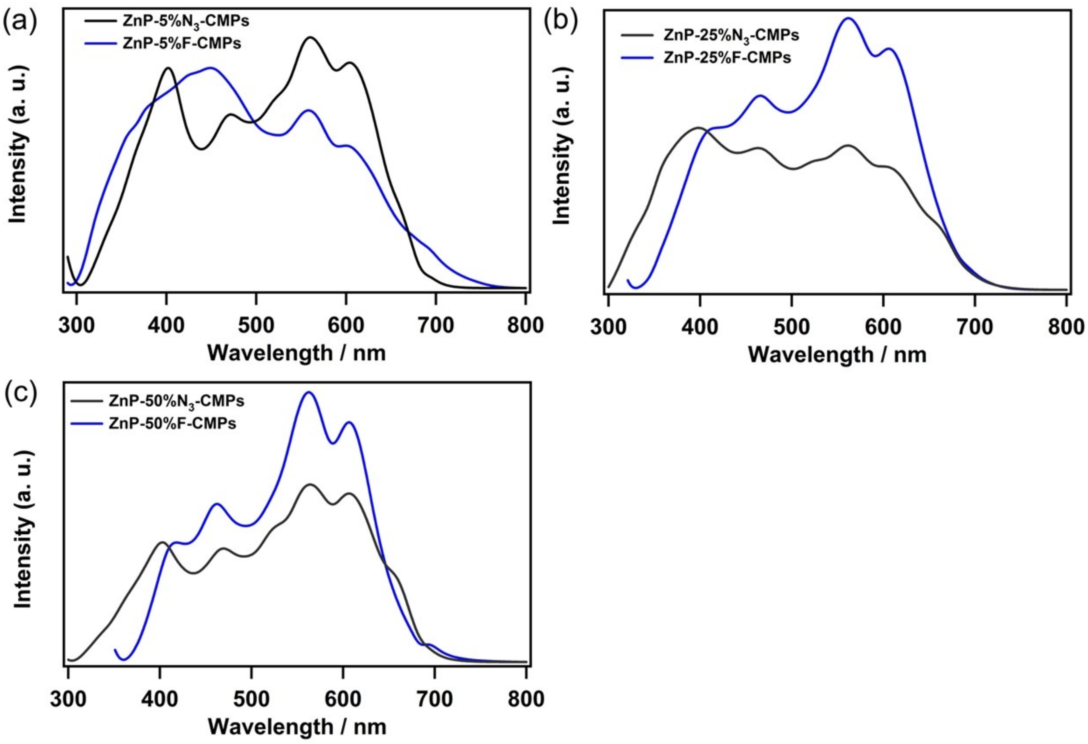


Fig. S7 UV-vis spectra of (a) ZnP-5%N$_3$-CMPs and ZnP-5%F-CMPs; (b) ZnP-25%N$_3$-CMPs and ZnP-25%F-CMPs; and ZnP-50%N$_3$-CMPs and ZnP-50%F-CMPs in the solid state.

Section H. Nitrogen isotherm profiles

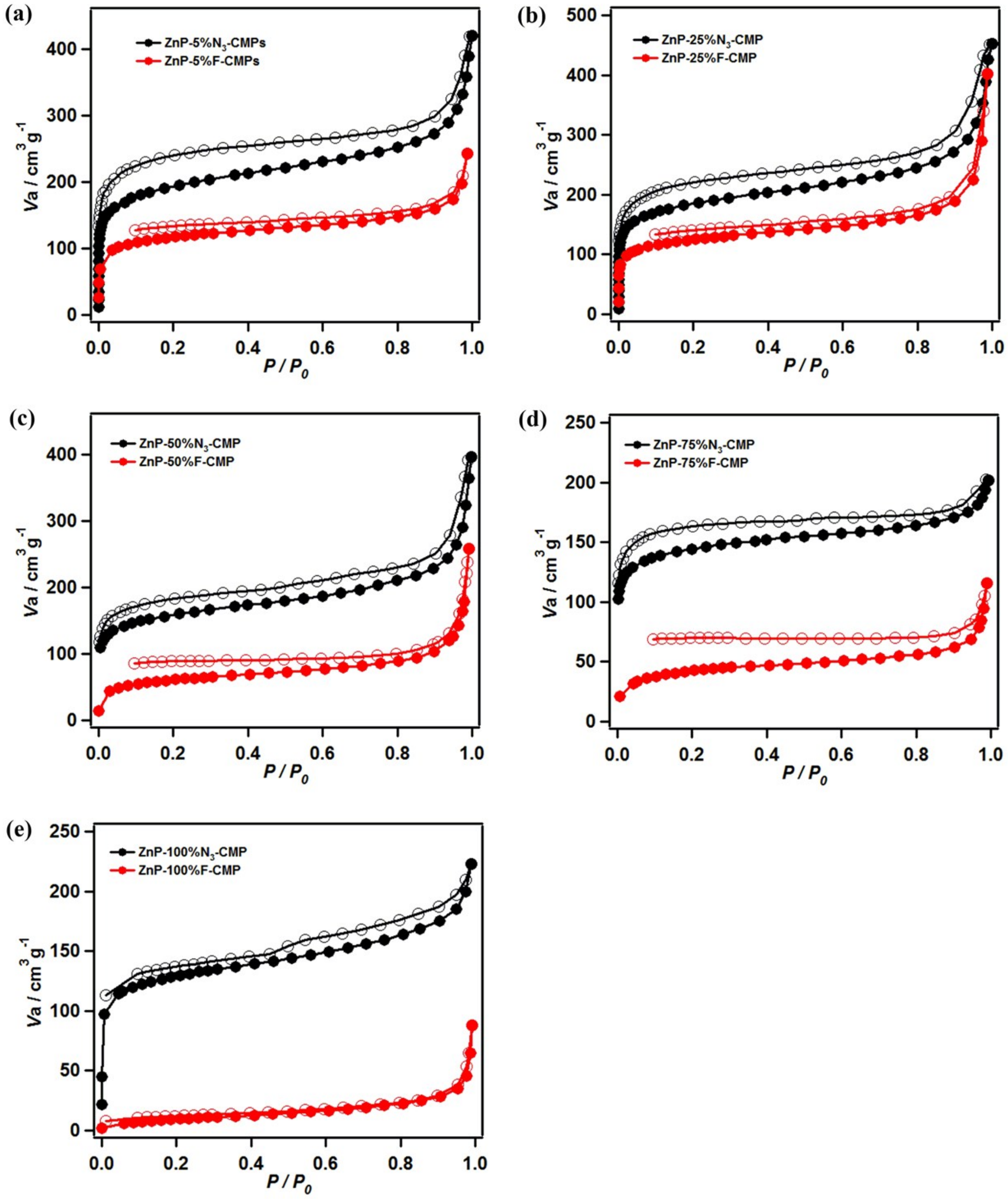


Fig. S8 Nitrogen adsorption and desorption isotherm profiles of ZnP-XN$_3$-CMPs (X= 5, 25, 50, 75, and 100%) and ZnP-XF-CMPs (X= 5, 25, 50, 75, and 100%).

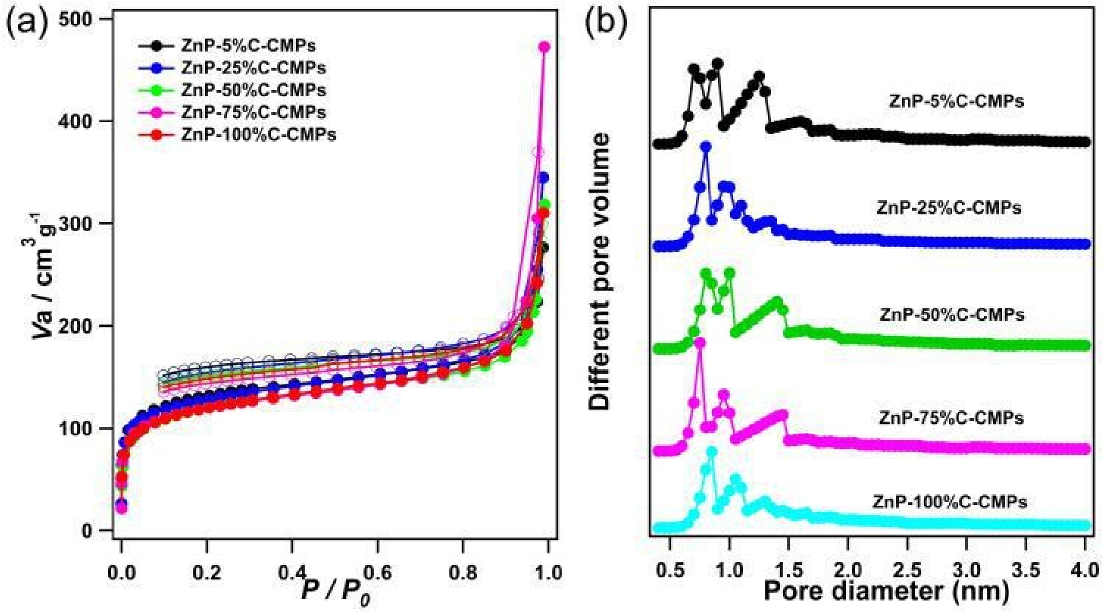


Fig. S9 Nitrogen adsorption (filled circle) and desorption (open circle) isotherm profiles of (a) ZnP-XC-CMPs (X= 5, 25, 50, 75 and 100%) measured at 77 k. Pore size distribution profiles of (b) ZnP-XC-CMPs (X= 5, 25, 50, 75 and 100%).

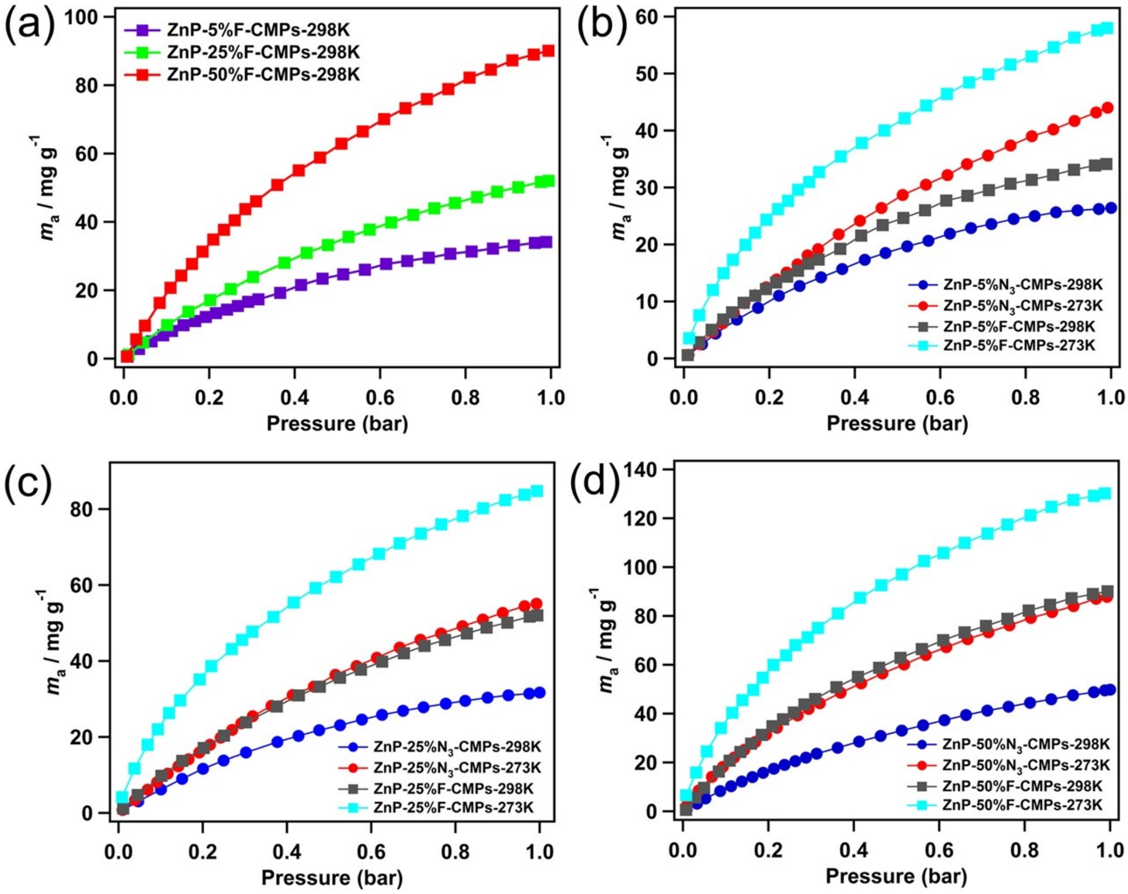


Fig. S10 CO$_2$ adsorption isotherms. (a) ZnP-XF-CMPs (X= 5, 25, and 50%) at 298 K and 1.0 bar; (b) ZnP-5%N$_3$-CMPs and ZnP-5%F-CMPs at 298 K/1.0 bar and 273 K/1.0 bar; (b) ZnP-25%N$_3$-CMPs and ZnP-25%F-CMPs at 298 K/1.0 bar and 273 K/1.0 bar; (d) ZnP-50%N$_3$-CMPs and ZnP-50%F-CMPs at 298 K/1.0 bar and 273 K/1.0 bar.

Section I. Isosteric heats of adsorption

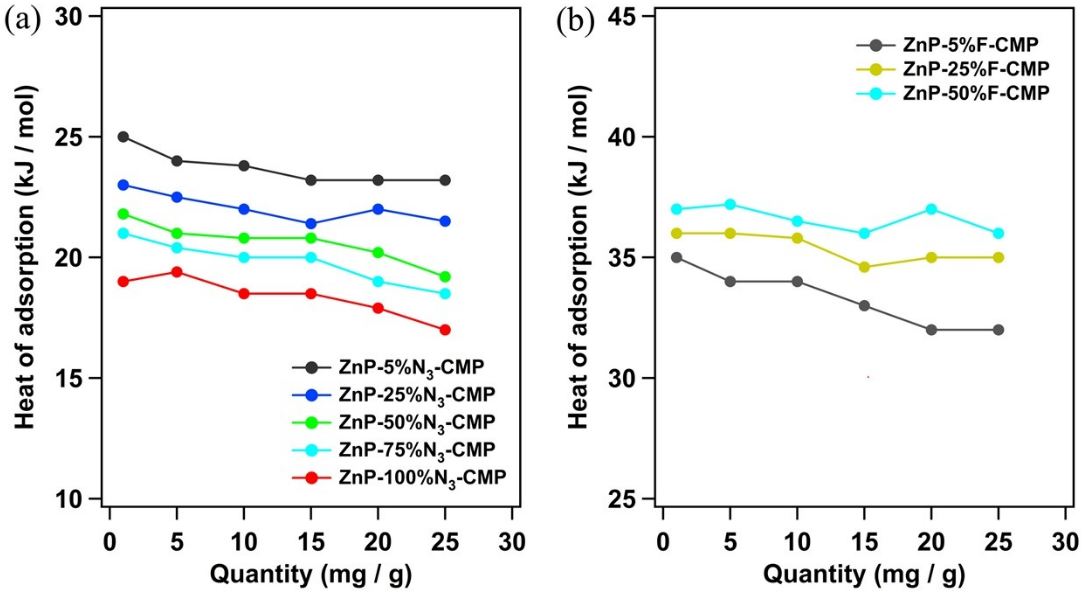


Fig. S11 Isosteric heats of adsorption of (a) ZnP-XN$_3$-CMPs (X= 5, 25, 50, 75, and 100%) and (b) ZnP-XF-CMPs (X= 5, 25, and 50%).

Table S1. Summary of Pore, Surface Properties and CO_2 adsorption capacity of Polymers.

Polymers	**S_{BET} (m^2/g)^a**	**V_{total} (cm^3/g)^b**	**CO_2 uptake (mmol/g)^c at 298 K**	**CO_2 uptake (mmol/g)^d at 273 K**
ZnP-5%N_3-CMPs	711	0.7659	26	44
ZnP-25%N_3-CMPs	685	0.7029	31	54
ZnP-50%N_3-CMPs	654	0.6812	49	87
ZnP-75%N_3-CMPs	565	0.4383	43	72
ZnP-100%N_3-CMPs	477	0.3446	40	69
ZnP-5%F-CMP	430	0.6767	34	58
ZnP-25%F-CMP	362	0.5211	52	84
ZnP-50%F-CMP	240	0.3762	90	130
ZnP-75%F-CMP	148	0.1790	–	–
ZnP-100%F-CMP	37	0.1187	–	–

[a]Calculated over the relative pressure range P/P_0 = 0.01 - 0.1. [b]Total pore volume (P/P_0 = 0.99).
[c]Data were obtained at 1.0 bar and 298 K. [d]Data were obtained at 1.0 bar and 273 K.

Table S2. Pore and Surface Properties of Polymers.

Polymers	**S_{BET} (m^2/g)^a**	**V_{total} (cm^3/g)^b**	**Pore Size**
ZnP-5%C-CMPs	483	0.4675	0.7 nm
ZnP-25%C-CMPs	468	0.5333	0.8 nm
ZnP-50%C-CMPs	426	0.4875	0.8 nm
ZnP-75%C-CMPs	430	0.4832	0.75 nm
ZnP-100%C-CMPs	435	0.4800	0.85 nm

[a]Calculated over the relative pressure range P/P_0 = 0.01 - 0.1. [b]Total pore volume (P/P_0 = 0.99).

Section J. Supporting references

S1 X. Liu, Y. Xu, Z. Guo, A. Nagai and D. Jiang, *Chem. Commun.,* 2013, **49**, 3233.

S2 L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong and D. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 9806.