Supplementary Information

for

Microporous organic polymers involving thiadiazolopyridine for high and selective uptake of greenhouse gases at low pressure

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I. Instrumentation and methods

Nuclear magnetic resonance (NMR) spectroscopy: The solution state ¹H and ¹³C NMR spectra were recorded on Bruker Avance III 500 MHz NMR spectrometers. The residual solvent signals were used as internal standard, and chemical shifts (δ) are reported in parts per million (ppm). The solid state ¹³C NMR experiments were carried out on JEOL ECX 400 MHz (field 9.4 T) standard bore spectrometer equipped with 4 mm solid-state MAS probe. The samples were packed into a 4 mm Zirconia rotor and spun at 8 kHz at the magic angle. The spectra were acquired with high power two-pulse phase modulation (TPPM) ¹H decoupling during the time of acquisition; a ramped amplitude cross polarization with a total sideband suppression (TOSS) sequence was used.

Fourier transform infra-red spectroscopy (FTIR): FTIR measurements were done on Perkin-Elmer Model 2000 FTIR using KBr pellet. Thirty scans were signal-averaged, with a resolution of 8 cm⁻¹ at ambient temperatures.

Electron spray ionization low resolution mass spectrometry (ESI-LRMS): ESI-LRMS was done on Bruker Daltonics MicroTOF-Q-II Mass Spectrometer using acetonitrile as solvent.

Thermogravimetric analysis (TGA): TGA was carried out using Perkin Elmer TGA-6000 instrument. The sample was heated from 30 °C to 900 °C under nitrogen atmosphere at a rate of 10 °C min⁻¹.

Powder X-ray diffraction (PXRD): PXRD experiment was done on PANalytical Empyrean XRD instrument. Data was collected for 2θ values ranging from 5° to 60°.

Field emission scanning electron microscopy (FESEM): The surface morphology of all polymers was examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope. Samples for microscopy were prepared by sprinkling (~ 0.5 mg) polymers (powdered form) on aluminium stub using silicon wafer over an adhesive carbon tape. All samples were coated with a thin layer of sputtered gold prior to imaging. FESEM was carried out using an accelerating voltage of 5 kV and 10 kV.

Energy dispersive X-ray spectroscopy (EDS): EDS was examined using a spectrometer (Oxford Instruments X-MaxN) attached to FESEM. Measurements were done at a working voltage of 20 kV and elemental Co was used as a reference.

Transmission electron microscopy (TEM): The morphology of TPMTP was examined using FEI TALOS 200S instrument at a working voltage of 200 kV. The samples for TEM analysis were prepared by drop casting a homogeneous dilute dispersion of TPMTP over a carbon coated 400 mesh Cu grid.

X-ray photo electron spectroscopy (XPS): The XPS experiment was performed on sample holder with a vacuum dried powder sample drop of the size 1.5 mm radius using PHI 5000 Versa Prob II, FIE Inc. The scan time was set for one hour per element for core level scan (energy band: 20 eV) with a pass setting of 23.5 eV, 0.025 eV step and 100 ms time per step for 5 cycles.

Gas adsorption studies: All the gas adsorption measurements were performed on Quantachrome Autosorb QUA211011 equipment. The temperature was maintained using chiller bath for measurements at 273 K and 298 K. Isotherms were analyzed using ASIQwin software. The heat of adsorption plots were obtained using ASIQwin software. All the samples were treated at a temperature of 80 °C for 24 h under high vacuum before the analysis.

Computational modeling: The computational modeling was carried out using the density functional theory (DFT) calculations with local spin density approximation (LSDA) consisting of Slater exchange and Volk-Wilk-Nusair correlation functional (RSVWN)¹ for the thiadiazolopyridine containing functional moiety of the TP-polymers to calculate the interaction distances.² The Gaussian 09 package and the 6-311+G* basis set was used for all the computations.^{3, 4} The binding affinity was further calculated by determining the difference in the total energies of the geometries at equilibrium of the native compounds with their complex.⁵

Binding energy $(E_b) = \{E(complex) - E(TP moiety) - E(CO_2)\}$

Where, E (*complex*), E (*TP moiety*) and E (*CO*₂) are the total energies of the TP moiety interacting with CO₂, only TP moiety and only CO₂ respectively.

II. Synthesis, characterization and physico-chemical properties of TPMTP

(a) Chemicals

All chemicals were used as received unless stated otherwise. 4,4'-Dibromobenzophenone, triphenylmethanol, ethynyltrimethylsilane, zinc-dust, tetrabutylammonium fluolride, triethylamine (99.5%), copper(I)iodide (99.995%), bis(triphenylphosphine)palladium(II) dichloride (98%), toluene (99.85%), diisopropylamine (99%) and tetrakis(triphenylphosphine)palladium(0) (99.9%) were received from Sigma-Aldrich. 1,3,5-Triethynylbenzene (98%) was procured from Alfa Aesar. Dichloromethane was received from Merck and was dried using calcium hydride and subsequently distilled. 1,3,5-Triethynylbenzene was further purified by washing through a silica gel column and subsequent recrystallizations.

(b) Synthesis of Monomers

(i) Synthesis of TETPM

The monomer TETPM was synthesized following a reported procedure.⁶



Scheme S1 Synthetic protocol of TETPM.

¹**H-NMR**: (400 MHz, CDCl₃) δ ¹H (ppm); 7.39 (8 H, d, *J* 8.5 Hz), 7.12 (8 H, d, *J* 8.5 Hz), 3.06 (4 H, s).

¹³**C-NMR**: (126 MHz, CDCl₃) δ ¹³C; 146.21, 131.67, 130.76, 120.30, 83.18, 77.62, 64.81.

MALDI-TOF: Calculated m/z for $C_{33}H_{20}$ [M⁺] 416.52, found 416.45.

(ii) Synthesis of 7-bromo-4-chloro-[1,2,5]-thiadiazolo-[3,4-c]-pyridine (BCTP)

The compound (BCTP) was synthesized following a reported procedure.⁷



Scheme S2 Synthetic protocol of BCTP.

¹H-NMR: (500 MHz, CDCl₃) δ ¹H (ppm); 8.55 (1 H, s).
¹³C-NMR: (126 MHz, CDCl₃) δ ¹³C; 156.21, 148.59, 145.31, 144.74, 111.00.
MALDI-TOF: Calculated m/z for C₅HBrClN₃S [M⁺] 250.50, found 250.10.

(c) Fabrication of TPMTP

In the typical synthesis of TPMTP, a mixture of TETPM (0.19 mmol), TP (0.38 mmol), CuI (0.076 mmol) and Pd(PPh₃)₄ (0.038 mmol) were degassed in a Schlenk tube. A mixture of dry DMF (4 mL) and anhydrous triethylamine (2 mL) were degassed using 3 cycles of freeze-pump-thaw and was added to the reaction mixture under inert atmosphere of argon. The reaction was allowed to continue for 48 h. Later, the reaction mixture was washed with MeOH (excess) and then filtered. The collected residue was further subjected to Soxhlet extraction using methanol, acetone and chloroform each for 24 h. The brownish red solid was collected and subjected to extensive drying. Yield: 85 %

(d) Characterization of TPMTP

(i) Fourier transform infra-red spectroscopy (FTIR)

The Fig. S1 is a comparison of FTIR spectra of the monomers along with the TPMTP polymer. It is noticeable that the sp C-H stretching of TETPM is absent in the polymer. In addition, the internal C \equiv C-H stretching of TETPM at 2100 cm⁻¹ shifted to 2200 cm⁻¹ as it is converted to C \equiv C-C. A broad peak at 3500 cm⁻¹ is due to the moisture adsorbed by the polymer.



Fig. S1 FTIR spectra of TPMTP comparing with the monomers TETPM and TP.

(ii) Solid state ¹³C CP-TOSS NMR spectroscopy of TPMTP

The solid state ¹³C NMR spectroscopy analysis of TPMTP (Fig. 1a) reveals the effective couplings between the monomers. The peaks at δ 84.19 and δ 98.94 ppm reveals the internal C=C attached to the co-monomer TP. The peak at δ 65.03 ppm further validates the incorporation of tetrahedral carbon in the polymer backbone.

TPMTP: ¹³C, δ/ ppm; 156.44, 147.66, 130.95, 121.06, 111.38, 98.94, 84.19, 65.03.

(iii) Powder X-ray diffraction (PXRD)

The powder X-ray diffraction analysis was carried out collecting at 2θ range of 5° to 60° . The broad pattern of the peak signifies the amorphous nature of the polymer.



Fig. S2 The PXRD pattern of TPMTP.

(iv) Microscopic characterizations of TPMTP

The field emission scanning electron microscopy (SEM) analysis of TPMTP further signifies the presence of granular morphology (Fig. S3). The EDS analysis was carried out at a working voltage of 20 kV using Co as reference (Fig. S4). Atomic and weight percentage of various elements obtained from the EDS analysis is listed in Table S1. Transmission electron microscopy analysis revealed porous nature of TPMTP (Fig. S5).



Fig. S3 FESEM images of TPMTP with different magnifications. Scale bar: (a) 1 µm and (b) 200 nm.

Sample	%	Carbon	Nitrogen	Sulfur
TDMTD	Wt.	67.89	29.62	2.49
	At.	72.05	26.96	0.99

Table S1 Atomic (At.) and weight (Wt.) % of carbon, nitrogen and sulfur acquired from EDS analysis.



Fig. S4 EDS profile of TPMTP.



Fig. S5 TEM images of TPMTP with different magnifications. Scale bar: (a) 100 and (b) 10 nm.

(v) Gas adsorption studies of TPMTP

(a) Nitrogen gas sorption and porosity

The nitrogen sorption isotherms of TPMTP indicate type I isotherm with a Brunauer–Emmett– Teller (BET) surface area of $870 \pm 20 \text{ m}^2 \text{ g}^{-1}$ for the different batches of the same polymer. The pore size distribution plots were estimated using the nonlocal density functional theory (NLDFT) method that confirms the microporous nature. The specific surface area plot for the TPMTP is also shown in the Fig. S6a. The plot is obtained by fitting the BET equation given as below.

$$\frac{P/P_0}{n\left(1-\frac{P}{P_0}\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} (P/P_0)$$

Where P/P_0 refers to the relative pressure, n_m refers to the specific monolayer capacity, n is the specific amount adsorbed at P/P_0 and C is the BET constant. The high value of C further confirms the presence of the narrow pores.⁸

The t-plot method was carried out using carbon-black as a standard to calculate the micropore volume, micropore area and the corresponding external surface area. The micropore volume was found to be 0.137 cm³ g⁻¹ calculated with the best fit range of P/P_0 (0.3-0.5) with a correlation coefficient of 0.999. The micropore and the external area were found to be 300 m² g⁻¹ and 590 m² g⁻¹ respectively (Fig. S6b).



Fig. S6 (a) The specific surface area plot and (b) the t-plot analysis showing the micropore area for TPMTP.

(b) CO₂ uptake and selectivity

The CO₂ adsorption isotherm collected at 298 K is shown in Fig. S7a; the same at 273 K was shown in Fig. 3a. The interaction of CO₂ with the network can be further elucidated by calculating the isosteric heat of adsorption (Fig. S7b). The isosteric heat of adsorption (Q_{st}) is the standard enthalpy of adsorption at fixed surface coverage. The Q_{st} values were calculated using the CO₂ adsorption isotherms collected at two different temperatures, say, 273 K and 298 K considering the fixed adsorbed amount at both the temperatures using the Clausius-Clapeyron equation, as given below.

$$ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

TPMTP was regenerated by drying at 353 K for 8 h for reusability (Fig. 3d). The CO₂ uptake was found to be similar for four cycles.



Fig. S7 (a) CO₂ uptake of TPMTP measured at 298 K and 1 bar. (b) Isosteric heat of adsorption profile of TPMTP.

(C) Selectivity calculations

(i) Ideal adsorbed solutions theory (IAST)

The CO₂/N₂ selectivity of the POPs under flue-gas conditions were estimated employing ideal adsorbed solution theory (IAST) model using experimental single-gas isotherms.⁹ In this context, the molar loadings in the mixture for the specified partial pressures in the bulk gas phase (0.85 bar for N₂ and 0.15 bar for CO₂) are best obtained through the fitting of the pure component isotherms.^{10, 11} Either a single-site Langmuir model (eq. 1) or a dual-site Langmuir model (eq. 2) can be used to fit the absolute component loadings, as indicated below.

$$q = \frac{q_{sat} \ b \ p}{1 + b \ p} \qquad \text{eq. 1}$$
$$q = q_A + q_B = \frac{q_{sat,A} \ b_A \ p}{1 + b_A \ p} + \frac{q_{sat,B} \ b_B \ p}{1 + b_B \ p} \qquad \text{eq. 2}$$

where, q and q_{sat} are the molar loading and saturation loading of the adsorbate (mol kg⁻¹), b is the parameter in the pure component Langmuir adsorption isotherm (Pa⁻¹) and subscripts A and B refer to two distinct adsorption sites. As there is no noticeable inflections in the N₂ and CO₂ adsorption isotherms at 273 K and 1 bar, the single-site Langmuir model was used for fitting.

The binary gas adsorption selectivity (S) was calculated employing the following equation.

Selectivity (S) =
$$\frac{q_1/q_2}{p_1/p_2}$$

where, q_1 and q_2 are the amount of adsorbate at pressure p_1 and p_2 respectively. The q_1 and q_2 values are taken from the fitting using the single-site Langmuir model. The fitting of the CO₂ and N₂ adsorption isotherms at 273 K and 1 bar for TPMTP is shown in Fig. S9. The relevant fitting data is shown in the inset of the figure. The CO₂/N₂ selectivity at 273 K and 1 bar for TPMTP was found to be 61.



Fig. S8 The selectivity of CO₂ over N₂ for TPMTP measured at 273 K and 1 bar. The continuous lines refer to the single-site Langmuir model fits for CO₂ and N₂ adsorption. Inset: the table depicting the q_{sat} and parameter b determined by the fitting of adsorption isotherms.

(ii) Initial slope method

The selectivity calculation by the initial slope method was estimated by considering the ratio of the initial slopes of the adsorption curves in the Henry's region.



Fig. S9 The selectivity of CO_2 adsorption over N_2 by TPMTP calculated by the initial slope method at 273 K and 1 bar.

(d) CH₄ and H₂ gas uptake by TPMTP



Fig. S10 (a) CH₄ adsorption isotherm measured at 273 K, 1 bar, (b) the selective CH₄ adsorption over N_2 by TPMTP and (c) selectivity of CH₄ over N_2 obtained from the initial slope method at 273 K and 1 bar.

The adsorbents with the pore sizes in the range of 0.7-1.2 nm with higher surface area are also potential materials for H₂ storage.¹² Owing to the microporous nature TPMTP shows H₂ uptake of 2.3 wt% (11.3 mmol g⁻¹, 254 cm³ g⁻¹) at 77 K and 1 bar (Fig. S11).



Fig. S11 The H₂ sorption profile of TPMTP measured at 77 K, 1 bar.

III. Fabrication and gas adsorption properties of TEBTP and TPETP

(a) Synthesis of TETPE

The monomer (TETPE) was synthesized following a reported procedure.¹³



Scheme S3 Synthetic protocol of TETPE.

¹H-NMR: (400 MHz, CDCl₃) δ ¹H (ppm); 7.27 (8 H, d, *J* 8.2 Hz), 6.94 (8 H, d, *J* 8.2 Hz), 3.07 (4 H, s).
¹³C-NMR: (126 MHz, CDCl₃) δ ¹³C; 143.42, 140.99, 131.93, 131.36, 120.85, 83.60, 77.94.
MALDI-TOF: Calculated for C₃₄H₂₀ [M⁺] 428.53, found 428.21.

(b) Fabrication of TEBTP

A mixture of TEB (0.19 mmol), TP (0.28 mmol), CuI (0.036 mmol) and Pd(PPh₃)₄ (0.019 mmol) were degassed in a Schlenk tube. A mixture of dry DMF (4 mL) and anhydrous triethylamine (2 mL) were degassed using freeze-pump-thaw cycles for three times and was added to the reaction mixture under the inert atmosphere of argon. The polymerization reaction was continued for 48 h at 120 °C. Later, the reaction mixture was washed with methanol (excess) and then filtered. The residue was subjected to Soxhlet extraction using methanol, acetone and chloroform, each for 24 h. The brownish red solid was collected and was dried for the subsequent analysis. Yield: 80 %



Scheme S4 The synthetic scheme depicting the fabrication of TEBTP.

(c) Fabrication of TPETP

The polymer TPETP was fabricated using the same protocol as that of TPMTP.



Scheme S5 The synthetic scheme depicting the fabrication of TPETP.

(d) Surface area, porosity and CO₂ uptake by TEBTP



Fig. S12 (a) N₂ sorption isotherms of TEBTP carried out at 77 K, 1 bar, (b) the specific BET surface area plot and (c) NLDFT pore size distribution of TEBTP calculated using N₂ sorption profile.



Fig. S13 (a) CO₂ sorption isotherms of TEBTP obtained at 273 K, 1 bar and (b) the isosteric heat of adsorption profile of TEBTP. (c) The selectivity of CO₂ over N₂ for TEBTP measured at 273 K and 1 bar. The continuous lines refer to the single-site Langmuir model fits for CO₂ and N₂ adsorption. Inset: the table depicting the q_{sat} and parameter b determined by the fitting of adsorption isotherms.

(e) Surface area, porosity and CO₂ uptake by TPETP



Fig. S14 (a) N₂ sorption isotherms of TPETP measured at 77 K, 1 bar, (b) the specific BET surface area plot and (c) NLDFT pore size distribution of TPETP calculated using N₂ sorption profile.



Fig. S15 (a) CO₂ sorption isotherms of TPETP carried out at 273 K, 1 bar and (b) the isosteric heat of adsorption profile of TPETP. (c) The selectivity of CO₂ over N₂ for TPETP measured at 273 K and 1 bar. The continuous lines refer to the single-site Langmuir model fits for CO₂ and N₂ adsorption. Inset: the table depicting the q_{sat} and parameter b determined by the fitting of adsorption isotherms.

POPs	CO2 loading at 15 kPa (mol kg ⁻¹)	N2 loading at 85 kPa (mol kg ⁻¹)	$S = (q_1/q_2)/(p_1/p_2)$
TPMTP	1.787	0.167	61
TEBTP	0.967	0.159	34
ТРЕТР	1.165	0.160	41

Table S2 The selectivity of CO_2/N_2 calculated by IAST method.

(f) XPS analysis of TP-based MOPs

The XPS analysis of TP-polymers is shown below. The thiadiazolic, phenylic and pyridinic entities are referred as Tz, Ph and Py respectively.



Fig. S16 XPS spectra of (a) N 1s and (b) C 1s of TPMTP.



Fig. S17 XPS spectra of (a) N 1s and (b) C 1s of TEBTP.



Fig. S18 XPS spectra of (a) N 1s and (b) C 1s of TPETP.

Table S3 XPS analysis of TP-polymers.

Sample	C 1s (phenylic) (283.28 eV)	C 1s (thiadiazolic) (284.56 eV)	N 1s (pyridinic) (398.94 eV)	N 1s (thiadiazolic) (397.93 eV)	
ТРМТР	57.0 %	42.9%	33.4%	66.5%	
ТЕВТР	48.8%	51.1%	34.1%	65.8%	
ТРЕТР	63.0%	36.9%	35.7%	64.2%	

IV. A comparative account of CO₂ uptake by TPMTP with notable POPs

Table S4 Comparison of surface area, CO₂ uptake (> 2.0 mmol g^{-1} at 273 K) and selectivity of tetraphenylmethane based POPs at 1 bar.

S. No.	S. No. Adsorbent		CO2 u mmol g	CO ₂ uptake		Ref.
		(m ² g ⁻¹)	273 K	298 K	_ (273 K, 1 bar)	
1.	TPMTP	890	5.8 (25.5)	3.6 (15.8)	61 ^a , 63 ^b	Present work
2.	PPN-6- CH2DETA	555	4.3 (19.0) 1.1 bar	3.6 (15.8), 295 K and 1.1 bar	442ª	Angew. Chem. Int. Ed., 2012, 51 , 7480. ¹⁰
3.	F-MOP-2	1031	5.0 (22.3)	1.5 (6.8)	-	<i>Chem. Commun.</i> , 2014, 50 , 13910. ¹⁴
4.	APOP-3	1402	4.5 (19.8)	2.6 (11.4)	27.5 ^a	Polym. Chem., 2013, 4 , 4690. ¹⁵
5.	BILP-1	1172	4.3 (18.9)	3.0 (13.0)	70 ^b	<i>Chem. Mater.</i> , 2011, 23 , 1650. ¹⁶
6.	MOPI-IV	660	3.8 (16.7)	2.3 (10.1)	43.4 ^a	<i>Chem. Mater.</i> , 2016, 28 , 5461. ¹⁷
7.	MPI-1	1454	3.8 (16.7)	2.2 (9.6)	102 ^b	<i>Macromolecules</i> , 2013, 46 , 3058. ¹⁸
8.	A ₆ CMP-6	1115	3.6 (15.8)	3.1 (13.6)	32.8 ^a	<i>Chem. Commun.</i> , 2016, 52 , 12602. ¹⁹
9.	MPI-6FA	781	3.1 (13.6)	2.0 (8.8)	49.6 ^b	<i>J. Mater. Chem. A</i> , 2016, 4 , 11453. ²⁰
10.	CPN-1-Cl	1504	2.9 (12.5)	-	-	<i>J. Mater. Chem. A</i> , 2014, 2 , 11825. ²¹
11.	Azo-COP-2	729	2.56 (11.2)	1.5 (6.7)	109 ^a	<i>Nat. Commun.</i> , 2013, 4 , 1357. ¹¹

12		556	25(112)			Chem. Commun., 2016, 52 ,		
12.	BB-FOF-3	550	2.3 (11.2)	-	-	12881. ²²		
12		156	22(0.7)			Chem. Commun., 2015, 51 ,		
15.	AZO-IVIOF-1	430	2.2 (9.7)	-	-	11576. ²³		
						ACS Appl. Mater.		
14.	Cz-TPM	713	2.2 (9.7)	1.3 (5.7)	35.6 ^a	Interfaces 2017, 9 ,		
						21438. ²⁴		
15		(())	2 0 (0 0)	1 2 (5 7)		Chem. Commun., 2014, 50 ,		
15.	HBC-POP-1	008	2.0 (9.0)	1.3 (5.7)	-	6171. ²⁵		
Calavia	Coloulated by ideal adaption theory (IAST) balaylated by the initial slope method							

^aCalculated by ideal adsorbed solution theory (IAST), ^bcalculated by the initial slope method.

Table S5 Comparison of surface area, CO₂ uptake (> 4 mmol g⁻¹ at 273 K) and selectivity of TPMTP with some of the best-known POPs at 1 bar.

S. No.	Adsorbent	Sbet (m ² g ⁻¹)	CO2 uptake mmol g ⁻¹ (wt%)		Selectivity Ref.	
		_	273 K	273 K 298 K		
1.	TPMTP	890	5.8 (25.5)	3.6 (15.8)	61 ^a	Present work
2.	TPETP	704	4.4 (19.4)	2.0 (8.8)	41 ^a	Present work
3.	HAT-CTF- 450/600	1090	6.3 (27.7)	4.8 (21.1)	183ª	J. Am. Chem. Soc., 2016, 138 , 11497. ²⁶
4.	PPF-1	1740	6.07 (26.7)	3.35 (14.7)	14.5 ^b	<i>Chem. Mater.</i> , 2013, 25 , 1630. ²⁷
5.	bipy- CTF600	2479	5.58 (24.6)	2.95 (13.0)	37 ^b	<i>Chem. Mater.</i> , 2015, 27 , 8001. ²⁸
6.	P-PCz	1647	5.57 (24.5)	2.97 (13.1)	32 ^b	<i>Chem. Commun.</i> , 2016, 52 , 4454. ⁵
7.	FCTF-1- 600	1535	5.53 (24.3)	3.41 (15.0)	19 ^a	<i>Energy Environ. Sci.</i> , 2013, 6 , 3684. ²⁹
8.	ALP-1	1235	5.37 (23.6)	3.25 (14.3)	35 ^b	<i>Chem. Mater.</i> , 2014, 26 , 1385. ³⁰

9.	TBILP-2	1080	5.19 (22.8)	3.32 (14.6)	40 ^a	<i>Macromolecules</i> , 2014, 47 , 8328. ³¹	
10.	BILP-3	1306	5.11 (22.5)	3.3 (14.5)	59 ^a	<i>Chem. Commun.</i> , 2012, 48 , 1141. ³²	
11.	CPOP-1	2220	4.82 (21.2)	2.82 (12.4)	25 ^b	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 6084. ³³	
12.	Zn@AB- COF	1120	4.68 (20.6)	1.79 (7.9)	48 ^b	<i>Chem. Mater.</i> , 2015, 27 , 7874. ³⁴	
13.	PCTF-4	1404	4.66 (20.5)	2.86 (12.6)	56 ^b	<i>Polym. Chem.</i> , 2015, 6 , 7410. ³⁵	
14.	Cz-POF-1	2065	4.59 (20.2)	2.93 (12.9)	19 ^b	<i>Chem. Mater.</i> , 2014, 26 , 4023. ³⁶	
15.	TNP4	1348	4.45 (19.6)	2.9 (12.7)	31 ^a	<i>J. Mater. Chem. A</i> , 2015, 3 , 23577. ³⁷	
16.	PPN-SO ₃ Li	1186	4.37 (19) @ 1.1 bar	3.7 (16.3) @ 295 K, 1.1 bar	414 ^a	<i>J. Am. Chem. Soc.</i> , 2011, 133 , 18126. ³⁸	
17.	CZ@PON	592	4.31 (18.9)	1.67 (7.3)	107 ^b	<i>Chem. Commun.</i> , 2017, 53 , 2752. ³⁹	
18.	HC-PCz-8	1688	4.3 (18.9)	3.5 (15.4)	16	<i>Chem. Commun.</i> , 2017, 53, 7645. ⁴⁰	
19.	BILP-1	1172	4.27 (18.8)	2.98 (13.1)	70 ^b	<i>Chem. Mater.</i> , 2011, 23 , 1650. ¹⁶	
20.	CPOP-9	2440	4.14 (18.2)	2.23 (9.8)	-	<i>Macromolecules</i> , 2014, 47 , 5926. ⁴¹	
^a Calculat	^a Calculated by IAST, ^b calculated by the initial slope method.						

Table S6 A brief comparative account of BET surf	ace area, N-functionality, N-content and CO ₂ uptake
capacity of few well-known N-containing POPs.	

S. No.	POPs	Sbet (m ² g ⁻¹)	Basic nitrogen functionality	N-content (wt. %)	CO ₂ uptake (mmol g ⁻¹) 273 K, 1 bar	Reference
1.	HAT-CTF- 450/600	1090	N N N N	35.23	6.3	Ref. 26
2.	PPF-1	1740	HC=N	9.83	6.07	Ref. 27
3.	TPMTP	890	N N	21.29	5.8	Present work
4.	P-PCz	1647		7.01	5.57	Ref. 5
5.	BILP-6- NH ₂	1185	H_{N}	20.68	5.56	Ref. 2
6.	ALP-1	1235	`N=N,	12.46	5.37	Ref. 30
7.	TBILP-2	1080	N N H	10.09	5.19	Ref. 31

8.	PPN-6- CH2DETA	555	H ₂ N NH ₂ H ₂ N H ₂ N	11.95	4.3 (1.1 bar)	Ref. 10
9.	PCTF-7	613		7.27	3.25	Ref. 42
10.	Azo-COP-2	729	`N=N,	14.4	2.56	Ref. 11



V. Nuclear magnetic resonance spectra of monomers

Fig. S19 ¹H NMR spectra of monomers: (a) TETPE, (b) TETPM and (c) BCTP.

(ii) ¹³C NMR spectroscopy



Fig. S20 ¹³C NMR spectra of monomers: (a) TETPE, (b) TETPM and (c) BCTP.

VI. References

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