Supporting Information

A triazine-based covalent organic polymer for efficient CO_2 adsorption

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Section S1: Experimental section

Materials:

4-aminobenzonitrile (MW=118.14), terephthaldehyde (MW=134.13) and trifluoromethanesulfonic acid were purchased from Sigma Aldrich, India. Anhydrous N,N-dimethylformamide was obtained from Spectrochem, India and used without further purification.

Synthesis of 1,3,5-tris-(4-aminophenyl)triazine (TAPT):

TAPT was synthesized via superacid catalyzed trimerization of 4-aminobenzonitrile. In a typical synthesis, 0.772 g (6.538 mmol) 4-aminobenzonitrile was taken in a round bottom flask at 0 ºC. Then 2 mL (22.2 mmol) trifluoromethanesulfonic acid was added dropwise for 20 min maintaining the temperature at 0 ºC. The resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, 20 mL distilled water was added to the mixture and it was neutralized by adding 2M NaOH solution until the pH reaches to 7. Initially, with increase in pH, the orange precipitate dissolves to give a bright orange solution, which upon further increase in pH gives a pale yellow precipitate. The resultant pale yellow product was filtered and washed several times with distilled water. The purified product was characterized by ^{1}H and ^{13}C NMR. Yield: 90.63 mol %

Synthesis of the covalent organic polymer TRITER-1

The polymer TRITER-1 was synthesized by Schiff base condensation reaction between TAPT and terephthaldehyde. In a typical reaction 709 mg (2 mmol) of TAPT and 402 mg (3 mmol) terephthaldehyde were taken in a two-neck round bottom flask fitted with a reflux condenser under N_2 atmosphere. To it 15 mL anhydrous DMF was added and the mixture was refluxed for 12 h. Then the solid product was filtered, washed with DMF and then with ethanol to remove any starting material present. Further the polymer was purified by Soxhlet extraction using methanol for 48 h. Yield: 83.72 wt%

Section S2: Characterization technique

N_2 adsorption/desorption isotherm of the sample was recorded using Quantachrome Autosorb 1C at 77 K. CO_2 adsorption isotherm of the material was recorded by using a Bel Japan Inc. Belsorp-HP at 273 K. Prior to both the measurement, the sample was degassed at 393 K for 12 h under high vacuum conditions. NLDFT pore-size distribution was obtained using N_2 at 77 K carbon cylindrical pore model of the Autosorb-1 software. The calculation involves complex mathematical modeling of fluid-solid and fluid-fluid interaction along with geometrical consideration (pore geometry) and thus it provides an accurate structure of fluid confined in the pores.[1] X-Ray diffraction patterns of the powder material were obtained in a Bruker AXS D-8 Advanced SWAX diffractometer using Cu-Kα (0.15406 nm) radiation. High resolution transmission electron microscopic (HR-TEM) image of the supermicroporous covalent organic polymer was obtained using a JEOL JEM 2010 transmission electron microscope operated at 200 kV. The sample was prepared by dropping a sonicated ethanol solution of the sample over a carbon-coated copper grid. Scanning electron microscopic measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope (FE-SEM). FT–IR spectra of the polymer TRITER-1 and the amine TAPT were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. The UV-Visible diffuse reflectance spectrum of the sample was recorded in a UV 2401PC with an integrating sphere attachment. $BaSO_4$ was used as the background standard. Solid-state MAS NMR studies have been performed by using Bruker Advance 500 MHz NMR spectrometer using a 4 nm MAS probe under static condition (spinning rate 5000 Hz, with sideband suppression). The ^1H and ^{13}C NMR spectra of the amine TAPT were recorded in a Bruker Advance 500 MHz NMR spectrometer. Mass spectrometric data of TAPT was acquired using the electron spray ionization (ESI) technique at 25–70 eV in a Micromass Q-tof-Micro

Quadruple mass spectrophotometer. Thermogravimetric analysis (TGA and DTA) of the sample was carried out between the temperature ranges from 308 to 873 K with a temperature ramp of 10 ºC/min in a TGA instrument thermal analyzer TA-SDT Q-600 under N_2 flow. Elemental analysis of the material was carried out using a Perkin Elmer 2400 Series II CHN analyzer.

Section S3: Wide angle powder XRD

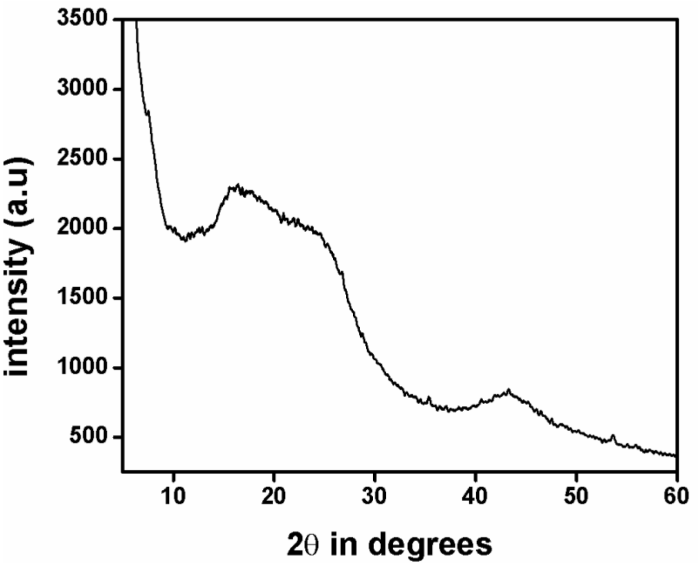


Figure S1. Wide angle powder X-ray diffraction pattern of TRITER-1

Section S4: Physico-chemical properties of TRITER-1

Table 1

Sample	d_{100} (nm)	a_{100} (nm)	S_{BET} (m^2g^{-1})	PD_{NLDFT} (nm)	PV (cm^3g^{-1})	WT (nm)
TRITER-1	2.99	3.45	716	1.7	0.32	1.75

d_{100} is the d(100) spacing.

a_{100} (unit cell parameter) = 2 $d_{100}/\sqrt{3}$.

S_{BET} = BET surface area.

PD_{NLDFT} is average pore diameter using NLDFT method.

PV is the total pore volume.

WT (wall thickness) = a_{100} - PD_{NLDFT}

Section S5: HR-TEM analysis

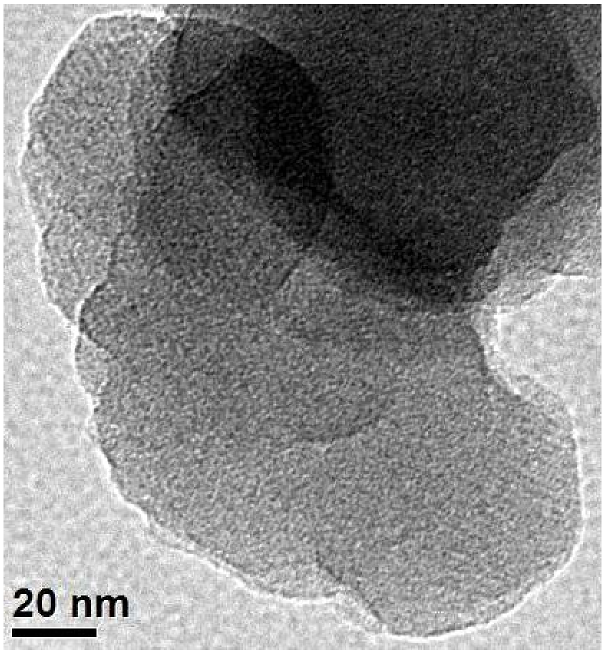


Figure S2. HR-TEM image of covalent organic polymer TRITER-1

Section S6: FE-SEM analysis

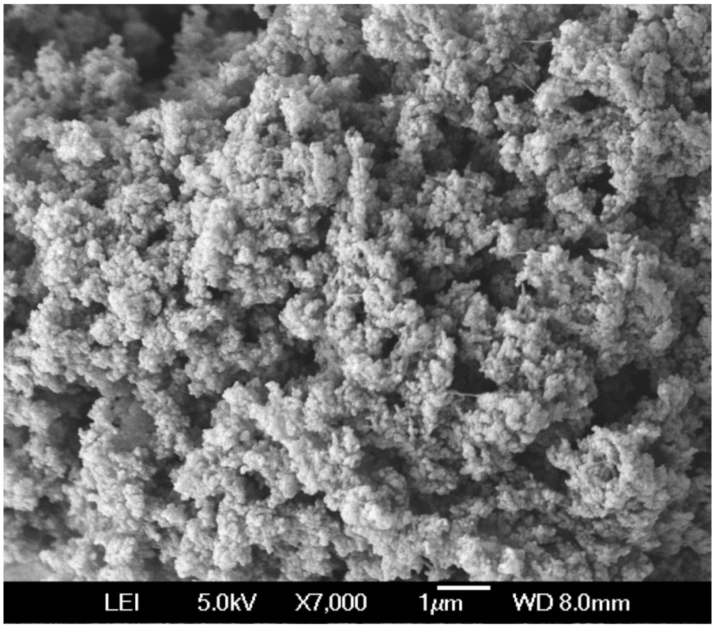


Figure S3. FE-SEM image of TRITER-1

Section S7: Unit cell parameters, indexing and molecular modeling of 2D hexagonal structure of TRITER-1

The experimental small angle PXRD has been matched with the theoretical PXRD pattern using REFLEX software.

Symmetry	Hexagonal
Lattice parameters	a=b=34.6, c=25, α=β=90º, γ=120º
Wavelength (Å)	1.54056
Range of data collection	0.4≤ 2θ ≤10

h	*k*	*l*	Theta (º)	2 Theta (º)	d
1	0	0	1.47303	2.94607	29.964
1	1	0	2.55193	5.10386	17.300
2	0	0	2.94704	5.89408	14.982

We have carried out the energy minimization for the hexagonal structure of TRITER-1 using chem.3D ultra 12.0 software. The resultant structure gives pore width of 3.1 nm and wall thickness 0.4 nm. Thus the summation of pore size and wall thickness is 3.5 nm and it matches closely with the unit cell parameter 3.45 nm (obtained from small angle PXRD). But from the HR-TEM image thick pore wall (black region in the image, 1.75 nm) can be seen which is of almost equal to the width with the pores (white region, 1.7 nm). A possible explanation for this is that the stacking between the 2D layers may not be perfectly of eclipsed AA type, and the triazine and terephthaldehyde moiety of one layer is not placed exactly above that of the next layer, which increases the wall thickness and decrease the pore width of the gross structure (as seen from the HR-TEM image). d100 is the spacing between the 100 planes, which includes the wall thickness, whereas the pore size obtained from HR-TEM and N_2 sorption analysis does not include the wall thickness. Due to thick pore wall (1.75 nm) of TRITER-1 the d100 and pore size is differing. The energy minimized single layer structure (left) and the proposed multi-layer stacking (right) is shown below.

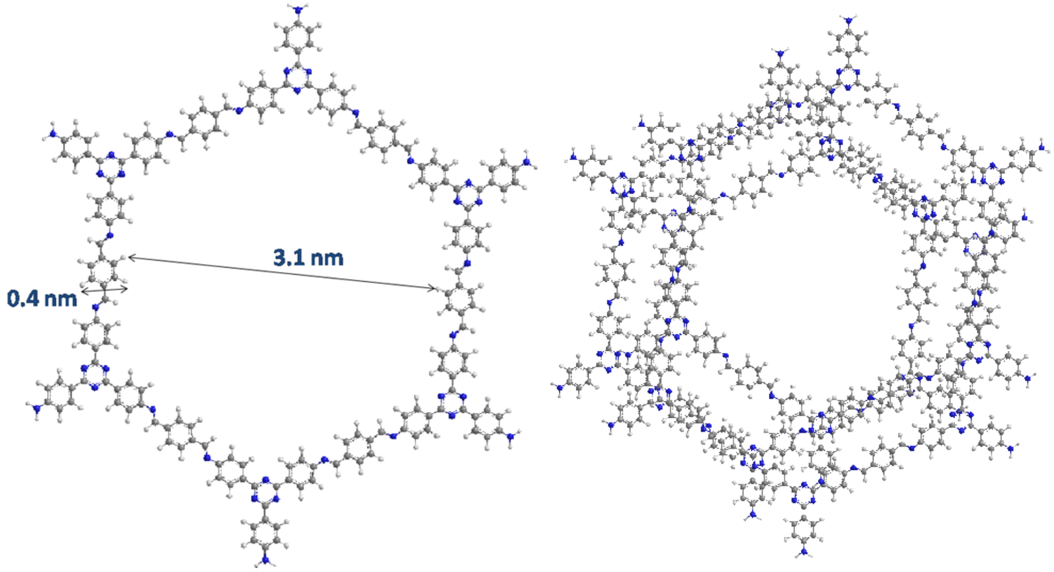


Figure S4: Molecular modeling of single (left) and multiple stacking planes (right) of 2D-hexagonal framework of TRITER-1.

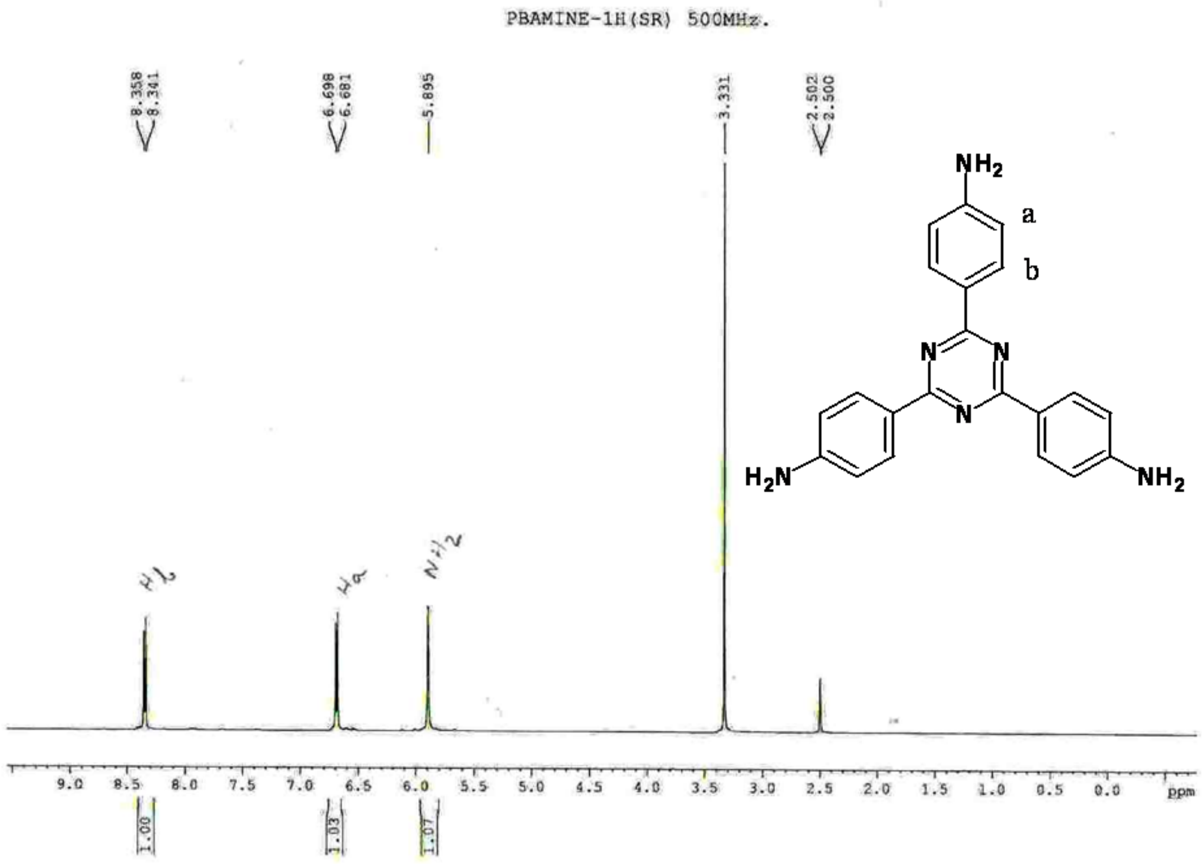
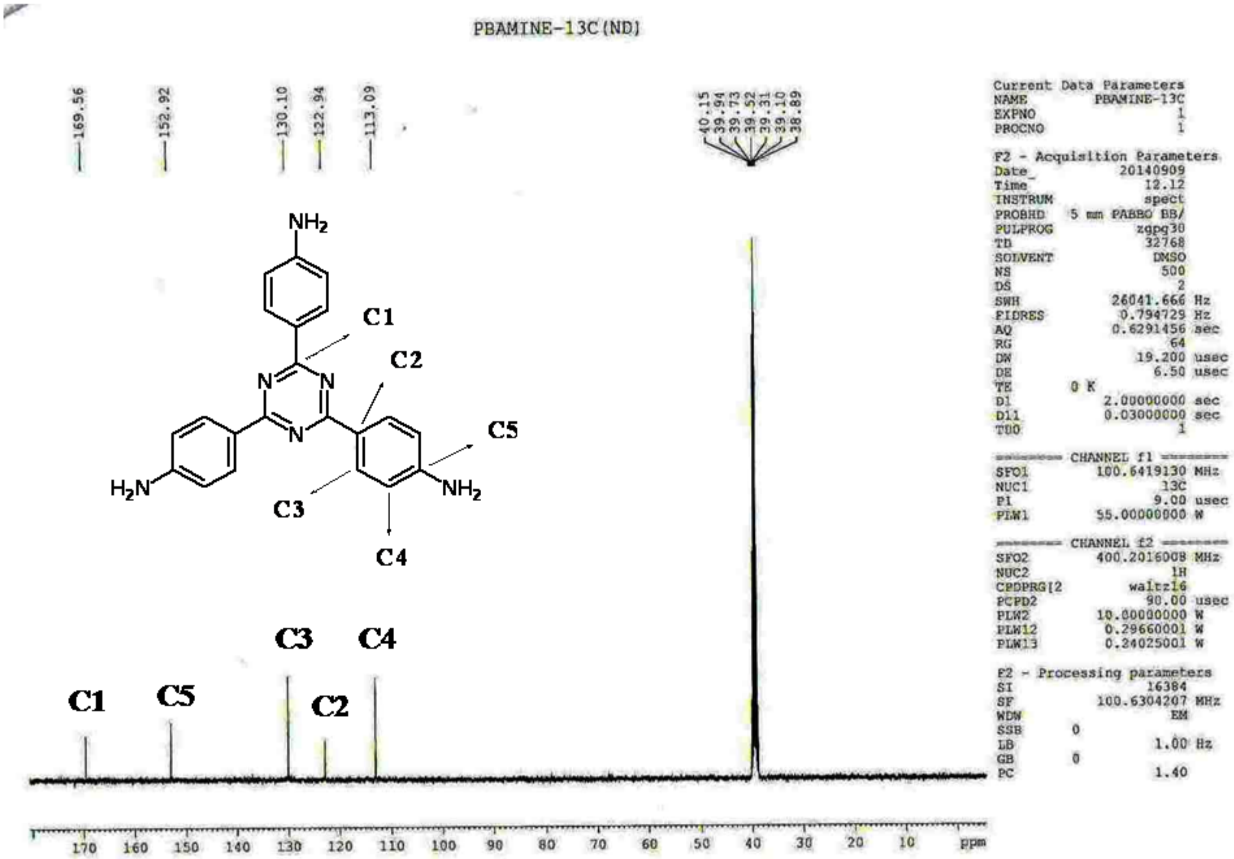


Figure S5. ^{1}H-NMR spectra of TAPT

^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm): 8.35 (d, J=8.5, 6H), 6.69 (d, J=8.5, 6H), 5.9 (s, 6H).

Section S9: ^{13}C-NMR spectra of TAPT



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Current Data Parameters
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EXPNO                  1
PROCNO                 1

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INSTRUM            spect
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PULPROG          zgpg30
TD                 32768
SOLVENT             DMSO
NS                   500
DS                     2
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             0.6291456 sec
RG                    64
DW                19.200 usec
DE                  6.50 usec
TE          0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6419130 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         55.00000000 W

======== CHANNEL f2 ========
SFO2         400.2016008 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         10.00000000 W
PLW12         0.29660001 W
PLW13         0.24025001 W

F2 - Processing parameters
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SF           100.6304207 MHz
WDW                   EM
SSB         0
LB                  1.00 Hz
GB          0
PC                  1.40
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Figure S6. ^{13}C-NMR spectra of TAPT

^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm): 169.6, 152.9, 130.1, 122.9, 113.1.

Section S10: Mass spectra of TAPT

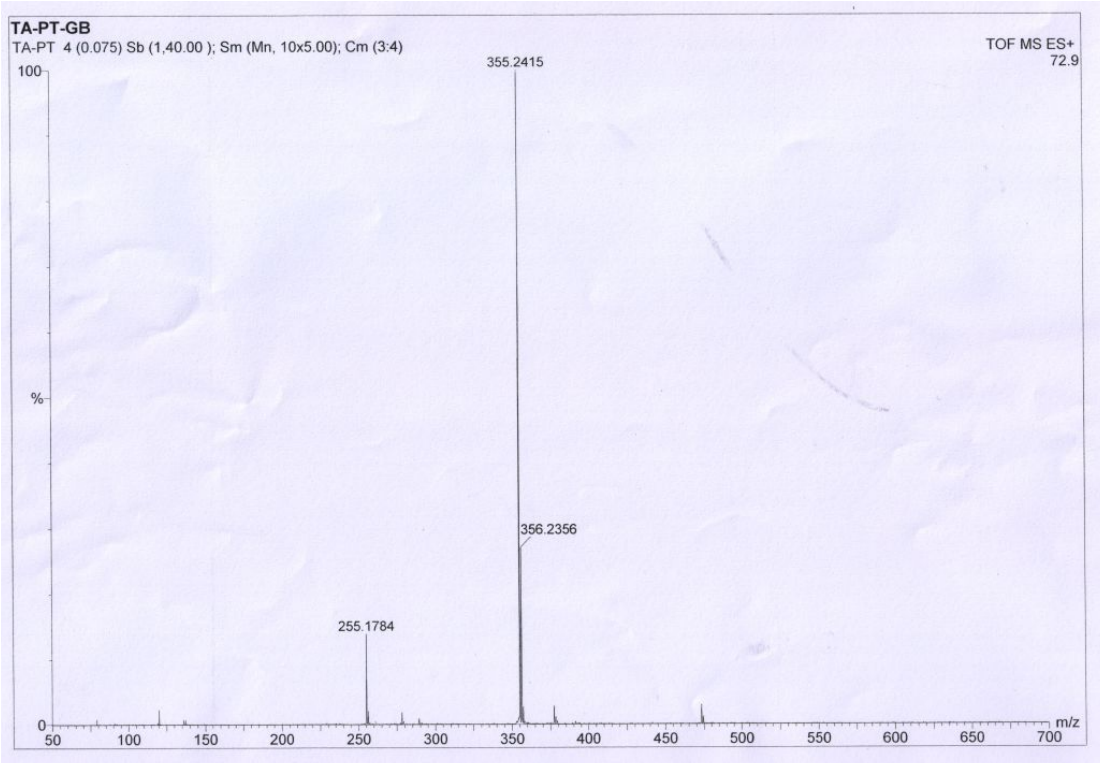

Figure S7. Mass spectra of TAPT

HR-MS *m/z*: 355.24 (M$^+$, calculated for $C_{21}H_{18}N_6$: 354.41)

Section S11: Infrared spectroscopy

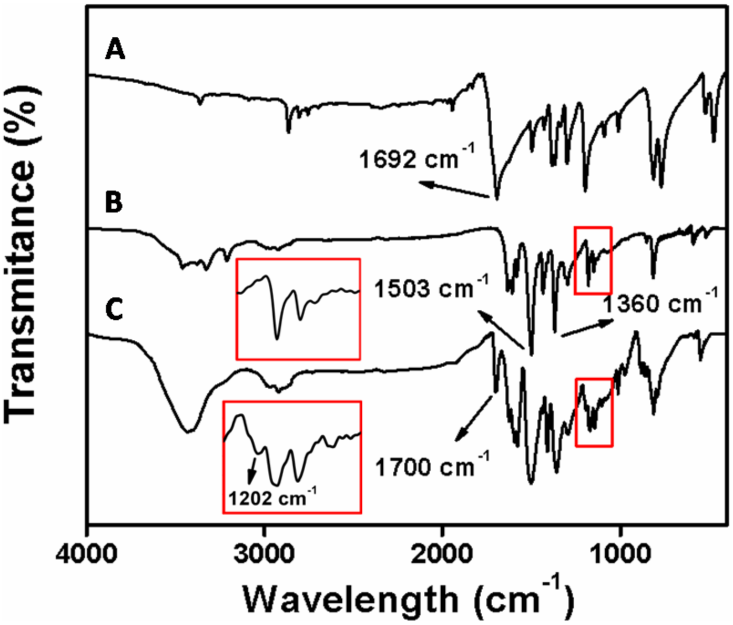

Figure S8. FT-IR spectra of terephthaldehyde (A), TAPT (B) and TRITER-1 (C)

Section S12: UV-Vis spectroscopy

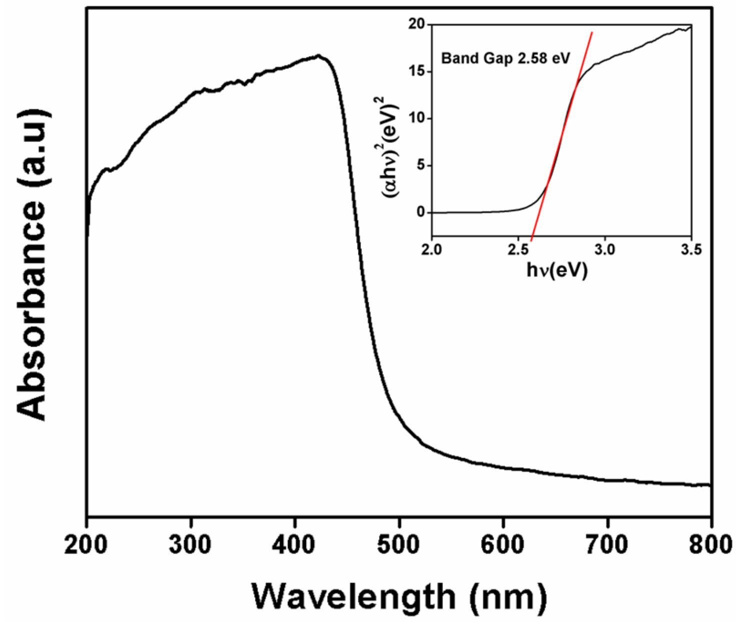

Figure S9. UV-Vis absorbance spectrum of TRITER-1 (Bandgap of the material is shown in inset)

Section S13: Thermogravimetric analysis

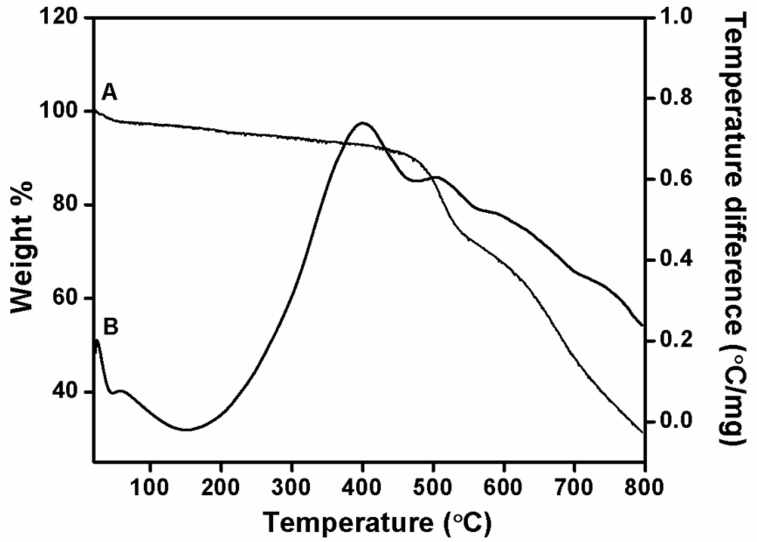

Figure S10. TGA (A) and DTA (B) plot of TRITER-1

Section S14: CHN analysis data of TRITER-1

Table 2

TRITER-1	C (%)	H (%)	N (%)
Experimental	78.67	3.99	16.03
Theoritical	79.04	4.19	16.77

Section S15: Isosteric heat of adsorption (Q_{st})

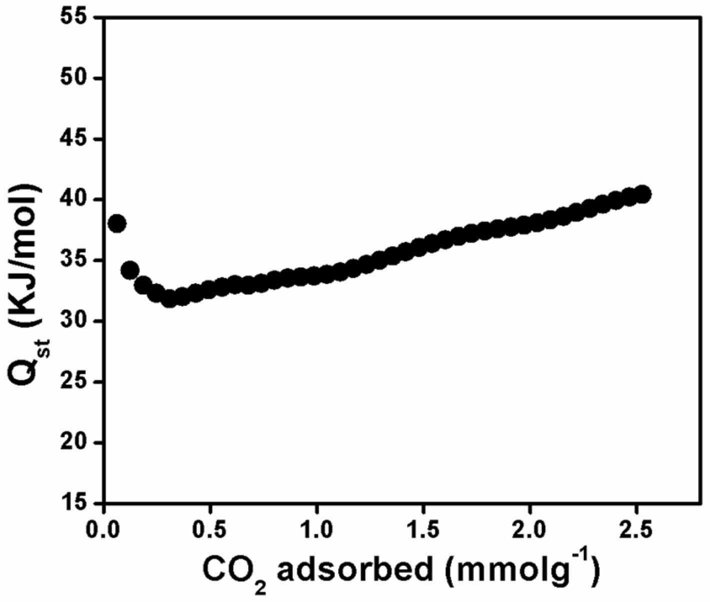

Figure S11. Isosteric heat of adsorption (Q_{st}) of TRITER-1 as a function of CO_2 adsorbed

Section S16: Recyclability test

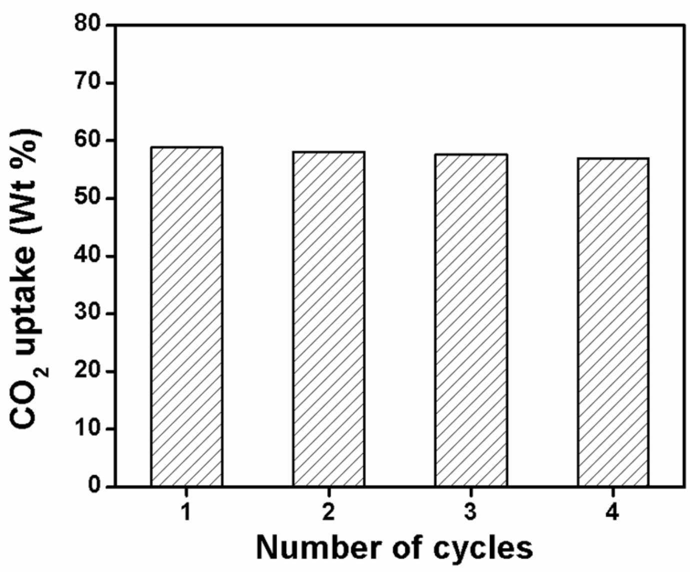

Figure S12. CO$_2$ adsorption capacity for recycled TRITER-1 at 273 K, 5 bar pressure.

Section S17: References

References

1 (a) P. I. Ravikovitcha, G. L. Hallera and A. V. Neimark, *Adv. Colloid Interface Sci.*, 1998, **76-77**, 203; (b) J. Jagiello and J. P. Olivier, *Carbon,* 2013, **55**, 70.