Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting information (ESI)

Porous graphene frameworks pillared by organic linkers with tunable surface area and gas storage properties

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Experimental Section

Materials: Sodium borohydride, 4-iodoaniline, sodium nitrate, 1,4-diiodobenzene, 4,4'diiodobiphenyl, trimethylsilyl acetylene, $Pd(PPh_3)_2Cl_2$, CuI, triethylamine, $Pd(PPh_3)_4$ were purchased from sigma Aldrich chemical co. and used without any further purification. 1,4diethynylbenzene, 4,4'-diethynylbiphenyl are prepared according to literature procedure¹. All the solvents used for synthesis were pre dried.

Synthesis of Graphite Oxide (GO): Graphite oxide was synthesized using modified hummers method.² In an ice bath 75 ml conc. H_2SO_4 was mixed with 1.5 g graphite powder and 1.5 g NaNO₃ and allowed to stir for 10 min. In the uniform mixture 10 g of KMnO₄ was added slowly and allowed to mix properly. The reactants were transferred to an oil bath maintained at 40 °C and stirred for another 45 min. To this mixture 75 ml distilled water was added followed by stirring for 15 min at 70 °C. Uniform brown color suspension was formed. The temperature was then raised to 80 °C and 15 ml H₂O₂ in 150 ml warm water (~70 °C) was added. The color of suspension changed from brown to yellow. Obtained product was centrifuged and washed repeatedly with deionized water. Graphite oxide was removed by centrifugation and obtained solid product was dried under vacuum at room temperature.

Preparation of reduced graphene oxide (RGO): Obtained graphite oxide was dispersed in water and reduced using NaBH₄ according to procedure reported in literature.³ Obtained product

has small concentration of residual epoxide, hydroxyl and carboxylic acid functional groups on basal plane and edges. N₂ adsorption isotherm of RGO has been determined (Fig. S10).

Preparation of RGO-IBz: Diazonium salt used for iodobenzene functionalization of graphene was prepared *in situ* using 4-iodoaniline.³ 960 mg (4.3 mmol) 4-iodoaniline was dissolved in 80 ml water by adding minimum amount of conc. HCl drop wise. 4-iodoaniline solution was then transferred to a round bottom flask maintained at 0 °C in an ice bath. To this solution 483 mg NaNO₂ (7 mmol) and 4 ml 20% HCl (6.4 M) was added and allowed to stir for 45 min. Color of the solution changed from transparent to yellow due to the formation of diazonium salt. Reduced graphene oxide obtained after sodium borohydride reduction was agglomerated with poor dispersion in water. RGO (125 mg) was dispersed in 125 ml 1 wt% sodium dodecylbenzene sulfonate (SDBS) surfactant solution. RGO dispersion was then added to diazonium salt solution. Reactant mixture was maintained at 0 °C for next 2 hours followed by stirring at room temperature for next 4 hours. Obtained product was filtered and washed with copious amount of water, (1:1) water-ethanol solution, ethanol and THF to remove the surfactant properly. Final product was dried in vacuum desiccator at room temperature.

Synthesis of PGF-1: In a typical procedure, mixture of RGO-IBz (40 mg), 1,4-diethynylbenzene (177 mg), Pd(PPh₃)₄ (3 mol%), CuI (6 mol%) were degassed by four freeze-thaw pump cycles and purged with N₂. To this 4 mL dry DMF and 1 mL anhydrous triethylamine were added under continuous N₂ flow. Reaction mixture is stirred at 140 °C for 48 hrs and cooled to room temperature. Precipitates were collected by filtration and washed several times with water, ethanol and THF. Further purification was carried out using soxhelet extraction technique with methanol and THF for 24 hrs each. Compounds were dried under vacuum at room temperature for 24 hrs. The obtained PGF samples were observed to be hydrophobic. Yield: 83%. FTIR in KBr (cm⁻¹): 3428(br), 3293(br), 3027(w), 2919(w), 2184(w), 1907 (w), 1664(br), 1600(s), 1502(m), 1384(m), 1261(w), 1178(w), 1099(s), 1016(m), 898(sh), 833(s), 543(w).

Synthesis of PGF-2: Similar procedure as of PGF-1 was adopted for the synthesis of PGF-2, except 4, 4'-diethynylbiphenyl was used as a linker. Yield: 78%. FTIR in KBr (cm⁻¹): 3438(br),

3299(br), 3029(w), 2919(w), 2184(w), 1909 (w), 1664(br), 1604(s), 1492(m), 138(m), 1261(w), 1178(w), 1099(s), 1004(m), 898(sh), 833(s), 543(w).

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Instrumentation

Infrared (IR) spectra were recorded using KBr pellets on a Bruker FT-IR spectrometer. Solid state ¹³C magic angle spinning (MAS) NMR spectrum was measured on a varian infinity plus 300 WB spectrometer at a MAS rate of 5 kHz and 11 kHz. Morphological studies have been carried out using Nova Nano SEM 600, FEI Company. Transmission Electron Microscopy (TEM) analysis has been performed using FEI TITAN3TM with an accelerating voltage of 80 kV to avoid beam induced damages. Thermo gravimetric analysis (TGA) was done using Mettler Toledo TGA 850 instrument in nitrogen atmosphere in the range of 30-900°C with a heating rate of 3 °C/ min. XP spectra were recorded in an Omicron Nanotechnology Spectrometer with Mg K α as the X-ray source. PXRD pattern of PGF-1 and PGF-2 were recorded in PANanlytical Empyrean using Cu K- α radiation. PXRD pattern of GO and RGO were recorded on Bruker D8 Discover using Cu K- α radiation.

Adsorption Measurements

The adsorption isotherm of N₂ (77 K), H₂ (77 K) and CO₂ (195 K, 273 K and 298 K) up to 1 atm for the sample of PGF-1 and PGF-2 were measured by using QUANTACHROME QUADRASORB-*SI* analyzer. In the sample tube the adsorbent sample (~100-150 mg) was placed which had been prepared at 433 K under a 1×10^{-1} Pa vacuum for about 6 h prior to measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated readily from pressure difference ($P_{cal} - P_e$), where P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed equilibrium pressure. All operations were computer-controlled and automatic.

High-pressure H_2 (77 K) and CO₂ (273 K) sorption isotherm measurements were carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. The hydrogen and CO₂ used for the high pressure measurements is scientific / research grade with 99.999% purity. For the measurements, approximately 200 mg sample was taken in a stainless-steel sample holder and degassed at 433 K for a period of 18 hours under 0.1 Pa vacuum. Dead volume of the sample cell was measured with helium gas of 99.999% purity. Non-ideal correction for hydrogen and carbon dioxide gas were made by applying virial coefficients at the respective measurement temperature.

The P_0 value used for adsorption measurements are 640 Torr for CO₂ at 195 K and 690 Torr for N₂ at 77 K. For H₂ uptake P_0 value used was 760 Torr. For all low pressure CO₂ uptake measurements done at 273 K and 298 K P_0 value used was 760 Torr.



Fig. S1 FTIR spectra for (a) RGO-IBz (black), (b) PGF-1 (blue) and (c) PGF-2 (red).



Fig. S2 ¹³C solid state NMR spectrum for PGF-2 at 5 kHz MAS.



Fig. S3 ¹³C solid state NMR spectrum for RGO at 5 kHz MAS.



Fig. S4 (a) High resolution I 3d XP spectra of RGO-IBz; (b) High resolution core level C1s XP spectra for (a) RGO-IBz and (b) PGF-1.⁴⁻⁶



Fig. S5 PXRD pattern of (a) PGF-1 (b) PGF-2 (c) GO (graphite oxide) and (d) RGO (reduced graphene oxide).



Fig. S6 (a, b) FESEM images of PGF-1, (c) TEM image of PGF-1; (d, e) FESEM images of PGF-2, (f) TEM image of PGF-2.



Fig. S7 TGA profiles for (a) RGO (black), (b) PGF-1(red) and (c) PGF-2 (blue) under N_2 atmosphere (flow rate 40 ml/min) with a heating rate of 3 °C/min.



Fig. S8 Pore-size distribution for PGF-1 based on NLDFT method calculated from N₂ adsorption isotherm at 77 K.



Fig. S9 Pore-size distribution for PGF-2 based on NLDFT method calculated from N₂ adsorption isotherm at 77 K.



Fig. S10 N_2 adsorption profile of (a) GO (graphene oxide, red), (b) RGO (reduced graphene oxide, black) at 77 K. GO and RGO have BET surface area of 14 m²/g and 42 m²/g respectively.



Fig. S11 CO₂ adsorption isotherms at 273 K (red) and 293 K (blue) of (a) PGF-1 and (b) PGF-2.



Fig. S12 H_2 adsorption isotherms for PGF-2 (blue) at 77 K and at 87 K (red). Inset, change of isosteric heat of adsorption versus uptake for PGF-2. Fitting parameter obtained from the Virial fitting given in table S1.



Fig. S13 Methane uptake at 195 K and 1 atm (a) PGF-1 (red) and (b) PGF-2 (blue).

Table S1: Fitting parameters obtained from the Virial fitting of two H₂ isotherms measured at 77 and 87 K for PGF-1 and PGF-2

Model		Virial (User)		
Equation		$y = \ln(x) + ((1/T)^*(a_0 + (a_1^*x) + (a_2^*x^{\wedge 2}) + (a_3^*x^{\wedge 3}) +$		
		$(a_4^*x^{\wedge 4}) + (a_5^*x^{\wedge 5}) + (a_6^*x^{\wedge 6}))) + (b_0 + (b_1^*x) +$		
		$(b_2^*x^{\wedge 2}) + (b_3^*x^{\wedge 3}))$		
Reduced Chi-Sqr				6.76431E-5
Adj. R-Square				0.99998
			Value	Standard Error
ln(P)/torr	a ₀		-963.47162	3.99308
	a ₁		84.73803	8.22954
	a ₂		-0.62746	4.6993
	a ₃		-6.53631	1.61601
	a 4		2.34401	0.48837
	a5		-0.34227	0.07122
	a ₆		0.01847	0.00395
	b ₀		13.969	0.04659
	b ₁		-0.35635	0.09489
	b ₂		0.07548	0.04936
	b ₃		-0.00584	0.0072
	Т		77	0
	Т		87	0

Model		Virial (User)		
Equatio	y = +	$y = \ln(x) + ((1/T)^{*}(a_{0} + (a_{1}^{*}x) + (a_{2}^{*}x^{^{2}}) + (a_{3}^{*}x^{^{3}}) + (a_{4}^{*}x^{^{4}}) + (a_{5}^{*}x^{^{5}}) + (a_{6}^{*}x^{^{6}}))) + (b_{0} + (b_{1}^{*}x) + (b_{2}^{*}x^{^{2}}) + (b_{3}^{*}x^{^{3}}) + (b_{4}^{*}x^{^{4}}))$		
Reduce	ed Chi-Sqr		0.03183	
Adj. F	R-Square		0.99332	
		Value	Standard Error	
ln(P)/torr	a ₁	-1046.34355	38.30645	
	a ₂	33.7413	9.81092	
	a ₃	-9.04943	2.8599	
	a4	0.75196	0.26867	
	b ₀	15.73052	0.45882	
	b ₁	-0.85578	0.18815	
	Т	77	0	
	Т	87	0	

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