

## ***Electronic Supplementary information (ESI)***

### **Assemblies of single-walled carbon nanotubes generated by covalent cross-linking with organic linkers**

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#### **Experimental section:**

**Chemicals:** Chemicals used for synthesis were of high purity and obtained from commercial sources. Solvents were pre dried before synthesis.

**Synthesis of 1,4-diethynylbenzene (linker 1):** The reaction was performed under nitrogen. In the mixture of 1,4-diiodobenzene (2g, 6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg), CuI (50 mg) and toluene (30 ml) at 80 °C trimethylsilylacetylene (2ml, 14 mmol) dissolved in 10 ml triethylamine was added dropwise and allowed to stir for 1 h. The product was diluted with ethyl acetate, passed through celite bed, washed with 1% NaHCO<sub>3</sub> aqueous solution, dried over anhydrous sodium sulphate, evaporated in rotary evaporator and purified by column chromatography (silica, hexane) to give 1,4-bis[(trimethylsilyl)ethynyl]benzene as an intermediate. (1.34 g, 82 %). The deprotection was carried out by stirring intermediate (1.25 g, 1equivalent) with K<sub>2</sub>CO<sub>3</sub> (5g, ~ 8 equivalents) in 35 ml methanol for 5 h. Excess methanol was evaporated in rotary evaporator, diluted with ethyl acetate, washed with water and dried over anhydrous sodium sulphate. Organic layer was dried in rotary evaporator to give 1,4-diethynylbenzene as the final product. (562 mg, 96%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 7.44 (s, 4 H; ArH), 3.16 (s, 2H; C≡CH).

**Synthesis of 4,4'-diethynylbiphenyl (linker 2):** 4,4'-Diethynylbiphenyl was prepared using the same procedure used for 1,4-diethynylbenzene. 4,4'-diiodobiphenyl (6 mmol) remaining reagents and condition same. (930 mg, 76.7 %) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 7.55–7.56 (m, 8 H; ArH), 3.14 (s, 2H; C≡CH).

**Iodobenzene functionalization of SWNT (SWNT-IBz):** Purified CoMoCat SWNTs (60 mg) were dispersed in 60 ml 1 wt% sodium dodecylbenzenesulfonate (NaDDBS) using sonication. In 50 ml water 4-iodoaniline (770 mg, 3 mmol) was dissolved by adding minimum amount of conc. HCl dropwise. Diazonium salt of 4-Iodoaniline was prepared by

adding  $\text{NaNO}_2$  (350 mg, 5 mmol) and 2.5 ml 20% HCl (6.4 M) and stirring for 45 min in an ice bath. Uniform SWNT dispersion was added to the *in situ* prepared diazonium salt and allowed to stir at ice bath temperature for 2 h followed by stirring at room temperature for next 4 h. Obtained product was filtered (0.45  $\mu\text{m}$ , nylon) and washed with water, (1:1) water-ethanol solution, ethanol and tetrahydrofuran to remove the surfactant properly. Final product was dried at 70 °C under vacuum.

**Synthesis of covalently cross-linked three dimensional assemblies of SWNTs:** In a schlenk flask SWNT-IBz (20 mg) was purged with nitrogen and sealed with septum. *N,N*-Dimethylformamide (DMF) (4ml) and triethylamine 4 ml was added and sonicated for 3 h. In the uniform dispersion  $\text{Pd}(\text{PPh}_3)_4$  (15 mg) and CuI (7 mg) was added under constant stirring and temperature was raised to 80 °C. In a separate vial 1,4-diethynylbenzene (100 mg) dissolved in 2 ml DMF was added dropwise to the reaction mixture, subsequently temperature was raised to 140 °C and allowed to stir for 24 h. Nitrogen atmosphere was maintained during the reaction. Precipitates were collected by filtration and washed properly with DMF and hexane. Further purification was carried out using Soxhlet extraction technique with methanol and hexane for 24 h each. Yield: 74 %. Elemental analysis (%) found: C 86.4, H 3.8. The product is designated ASWNT-1. The same procedure was used for obtaining ASWNT-2 except 4,4'-diethynylbiphenyl was used as the linker. Yield: 71%. Elemental analysis (%): C 85.7, H 4.2.

**Characterization:** Raman spectra were collected at several different spots in backscattering geometry using HORIBA LabRam HR800. FTIR spectra were recorded attenuated-total-reflectance accessories in a Bruker FT-IR spectrometer. Solid state  $^{13}\text{C}$  magic angle spinning (MAS) NMR spectrum was collected on a Bruker 400 MHz spectrometer. Morphological studies were carried out using Nova Nano SEM 600, FEI Company. Transmission Electron Microscopy (TEM) analysis was performed using the FEI Tecnai with an accelerating voltage of 200 kV. Thermo gravimetric analysis (TGA) was done using Mettler Toledo TGA 850 instrument in nitrogen atmosphere in the temperature range of 30 – 700 °C with a heating rate of 3 °C/ min. XP spectra were recorded in an Omicron Nanotechnology Spectrometer with Mg  $K\alpha$  as the X-ray source. PXRD pattern was recorded in PANalytical Empyrean using Cu  $K\alpha$  radiation. Elemental analysis was performed using Thermo Scientific Flash 2000 Elemental Analyzer.

The adsorption isotherms of N<sub>2</sub> (77 K), H<sub>2</sub> (77 K), CO<sub>2</sub> (195 K, and 293 K) up to 1 atm were obtained by using QUANTACHROME QUADRASORB-SI analyzer. The sample was heated at 433 K under vacuum for about 12 h prior to the measurement of isotherms. The adsorbate was charged into the sample tube and change in pressure was monitored. The degree of adsorption was determined by monitoring the decrease in pressure at the equilibrium state. All operations involved in sorption experiment were computer controlled and automatic.

Pore size distribution was calculated by non-local density functional theory (NLDFT) using ASiQwin 3 software provided by Quantachrome instruments for the characterization of porous materials. Density Functional Theory (DFT) gives a more realistic sorption and phase behavior of fluids in narrow pores on a molecular level and is considered a reliable method for pore size analysis. The non-local density functional theory (NLDFT) correctly explains the local fluid structure near curved solid walls. The adsorption isotherms in model pores are obtained by using the intermolecular potentials of the fluid-fluid and solid-fluid interactions. The relation between isotherms determined by NLDFT and the experimental isotherm on a porous solid is given by generalized adsorption isotherm (GAI) equation:

$$N\left(\frac{P}{P_0}\right) = \int_{w_{min}}^{w_{max}} N\left(\frac{P}{P_0}, w\right) f(w) dw$$

Where

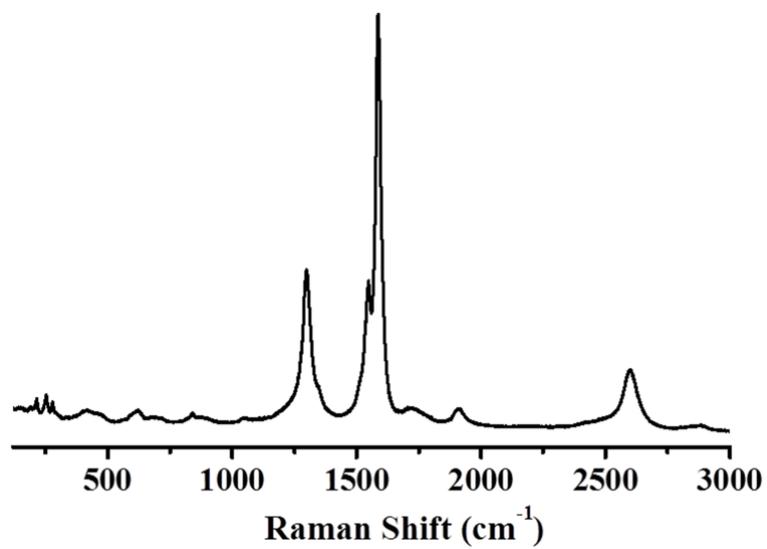
$N(P/P_0)$  = experimental adsorption isotherm

$w$  = pore width

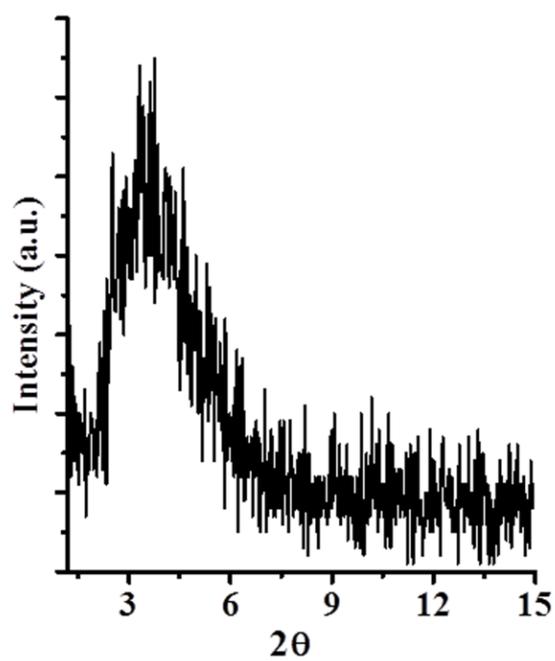
$N(P/P_0, w)$  = isotherm on a single pore of width  $w$

$f(w)$  = pore size distribution function

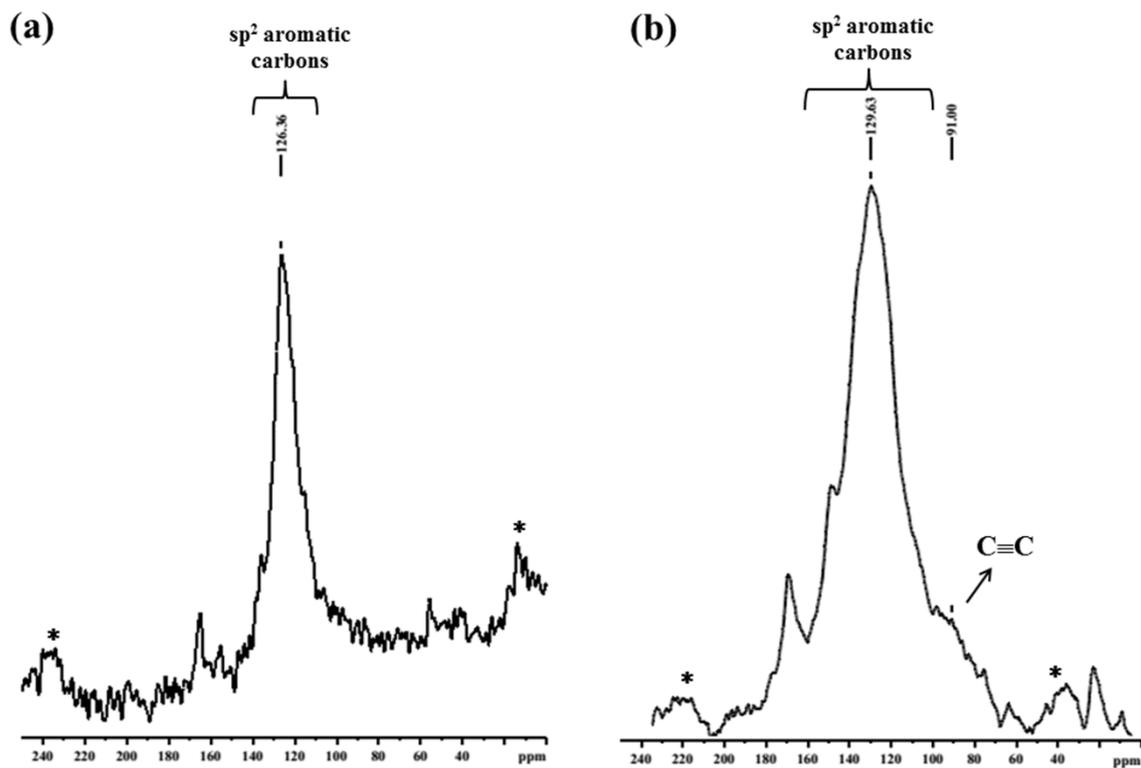
In GAI equation it is assumed that the total isotherm consists of a number of individual “single pore” isotherms multiplied by their relative distribution,  $f(W)$ , over a range of pore sizes. The set of  $N(P/P_0, w)$  isotherms for a given system (adsorbate/adsorbent) is obtained by density functional theory and is available as kernel files with the software. The pore size distribution is obtained by solving the GAI equation numerically via a fast non-negative least square algorithm.



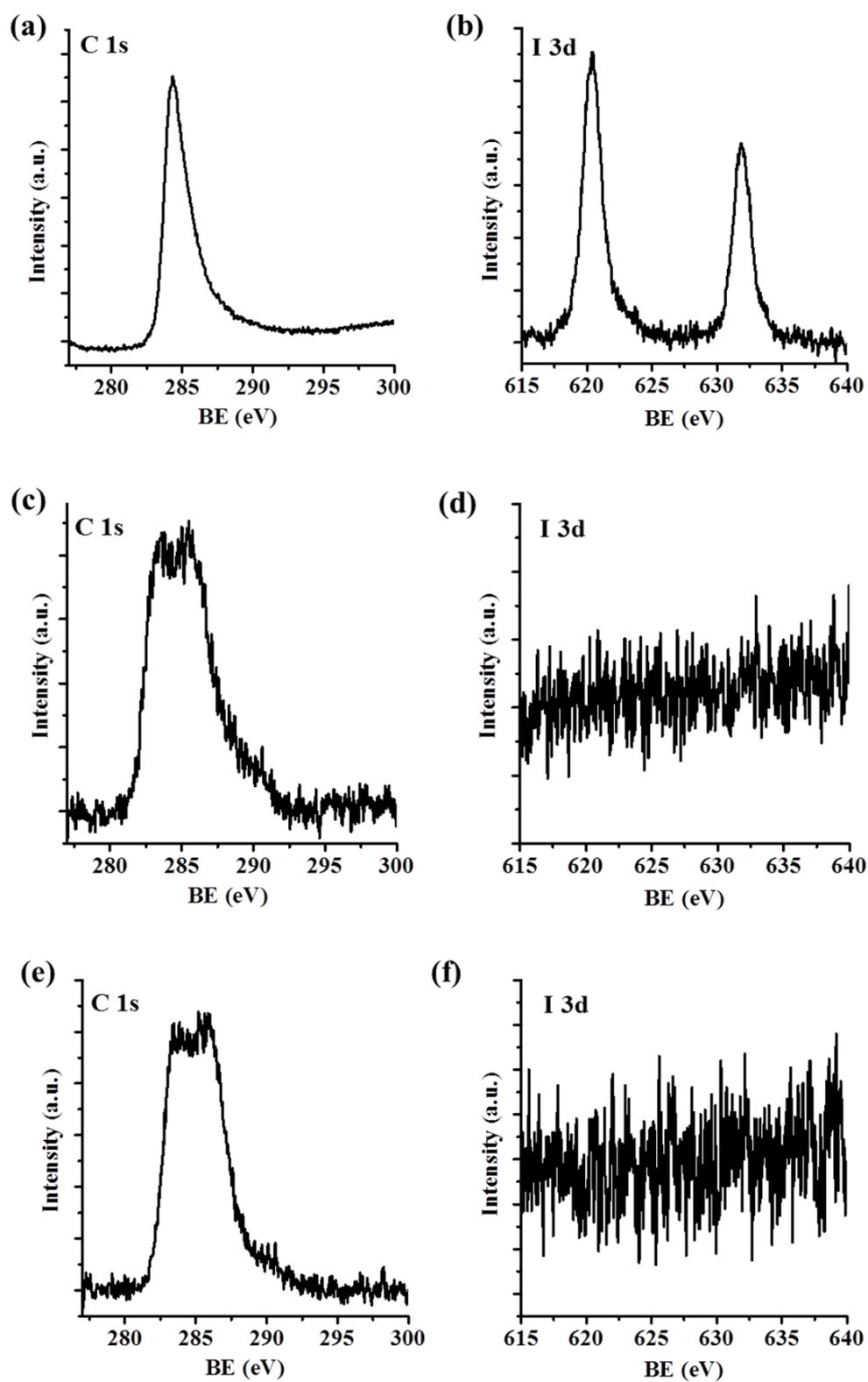
**Fig. S1** Raman spectrum of iodobenzene functionalized SWNT.



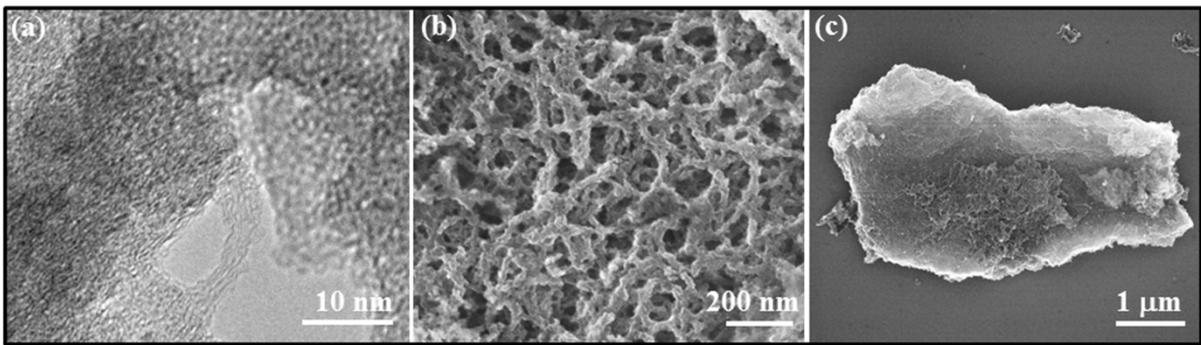
**Fig. S2** PXRD pattern of ASWNT-2.



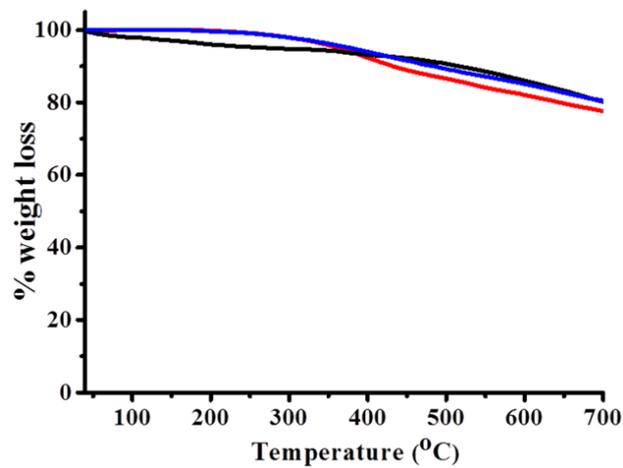
**Fig. S3** Direct pulse  $^{13}\text{C}$  solid state NMR spectra of (a) SWNT and (b) ASWNT-1 at 11 kHz MAS. Asterisks represents spinning side bands.



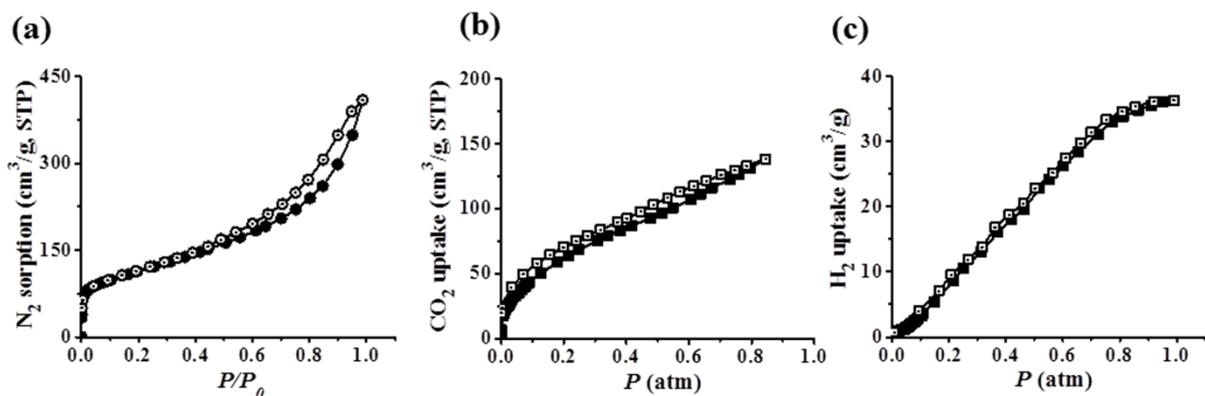
**Fig. S4** High resolution C 1s and I 3d X-ray photoelectron spectrum of (a, b) Iodobenzene functionalized SWNT (SWNT-IBz); (c, d) ASWNT-1 and (e, f) ASWNT-2.



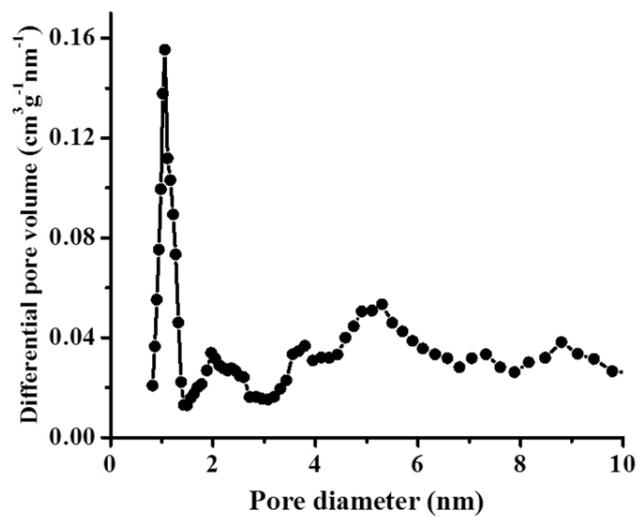
**Fig. S5** (a) TEM image of ASWNT-2. FESEM image of (b) ASWNT-2 and (c) typical monolith of three-dimensional ASWNTs assemblies obtained after covalent crosslinking (present image of ASWNT-2).



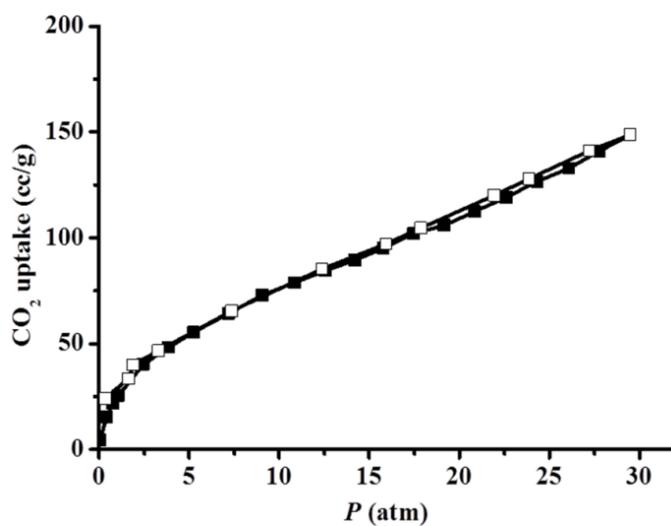
**Fig. S6** TGA profile of (a) SWNT (black), (b) ASWNT-1 (blue) and ASWNT-2 (red) in  $N_2$  atmosphere (flow rate 40 ml/min) with a heating rate of 3 °C/min.



**Fig. S7** Sorption profiles of pristine SWNTs (a)  $N_2$  at 77 K; (b)  $CO_2$  195 K and (c)  $H_2$  at 77 K.



**Fig. S8** Pore size distribution of pristine SWNT calculated by NLDFT.



**Fig. S9** High pressure CO<sub>2</sub> sorption profile of ASWNT-1 at 273 K.

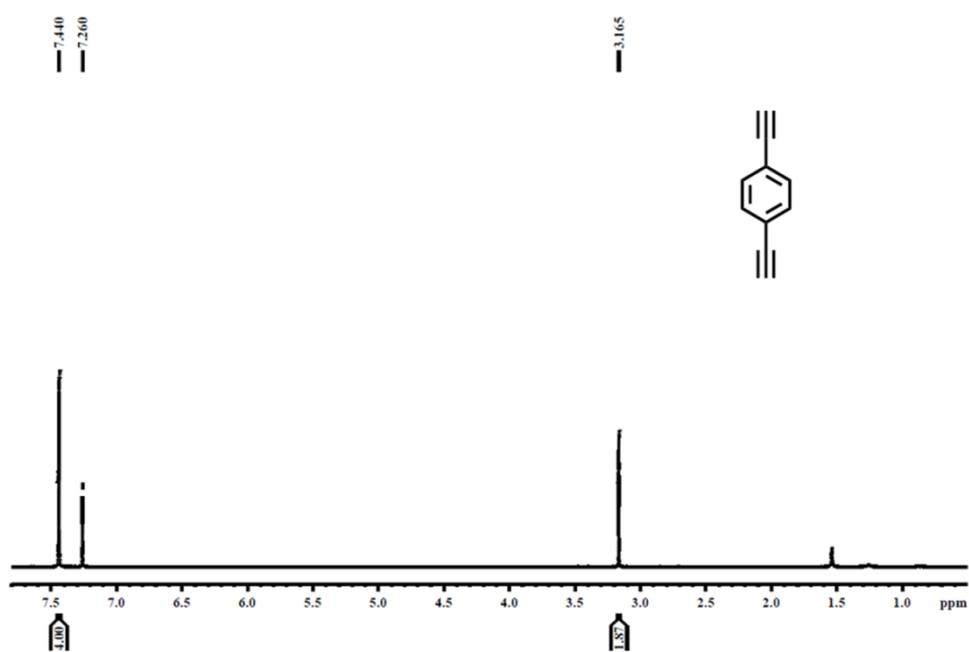


Fig. S10 NMR spectrum of 1,4-diethynylbenzene

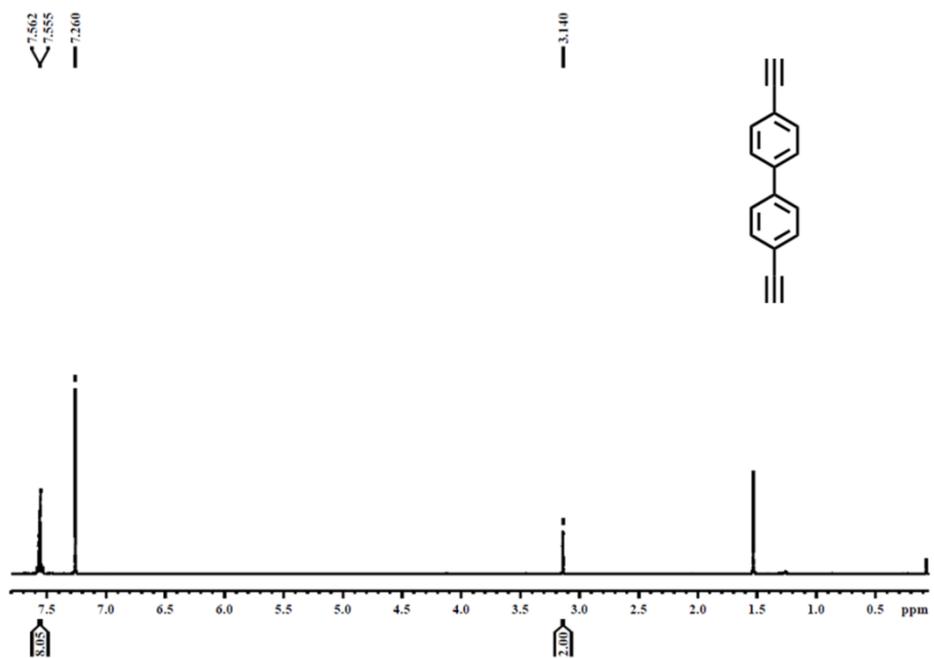


Fig. S11 NMR spectrum of 4,4'-diethynylbiphenyl.