Electronic Supplementary Material (ESI) for RSC Advances.

Diazapyrenium-based porous cationic polymers for colorimetric amine sensing and capture from CO_2 scrubbing conditions

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Electronic Supplementary Information

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1. General Methods

Materials. The solvents and reagents were purchased from Sigma-Aldrich, TCI or ACROS and used without purifications. 1,3,5-tris(bromomethyl)benzene was purchased from Sigma-Aldrich. 2,7-diazapyrene and was prepared by following previously reported procedure.[1]

Characterization Methods. FT-IR spectra were recorded on ATR mode by using Shimadzu FTIR Spectrometer by averaging 200 scans with a resolution of 2 cm^{-1}, measuring in transmission mode. The scanning electron microscopy (SEM) and energy dispersive X-ray absorption spectroscopy (EDS) analyses were carried out by using a Hitachi S-4800 FE-SEM at 15 kV. All the samples were attached on carbon tapes. Powder X-ray diffraction (PXRD) patterns of the samples were acquired from 3° to 80° by a Rigaku D/MAX-2500 at a generator voltage of 40 kV and a generator current of 300 mA. Elemental analysis (C, H, N) was done on a FlashEA 2000 (Series) [C, H, N, S] Elemental Analyzer, the sample was degassed prior to the analysis. Thermogravimetric analysis was performed by using a NETZSCH-TG 209 F3 instrument and the samples were heated to 800^{o}C at a rate of 10^{o}C min^{-1} under N_2 atmosphere. Solid-state cross polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra of polymers were taken using Bruker Digital Avance III HD 400 WB (400 MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 7.0 kHz. The Ar adsorption and desorption isotherms were measured at 87 K by using Micrometrics 3-Flex Surface Characterization Analyzer. The samples were degassed at 100^{o}C for 6 h under vacuum prior to the analysis. The surface areas of samples were calculated using BET model in the pressure range determined from the Rouquerol plot.

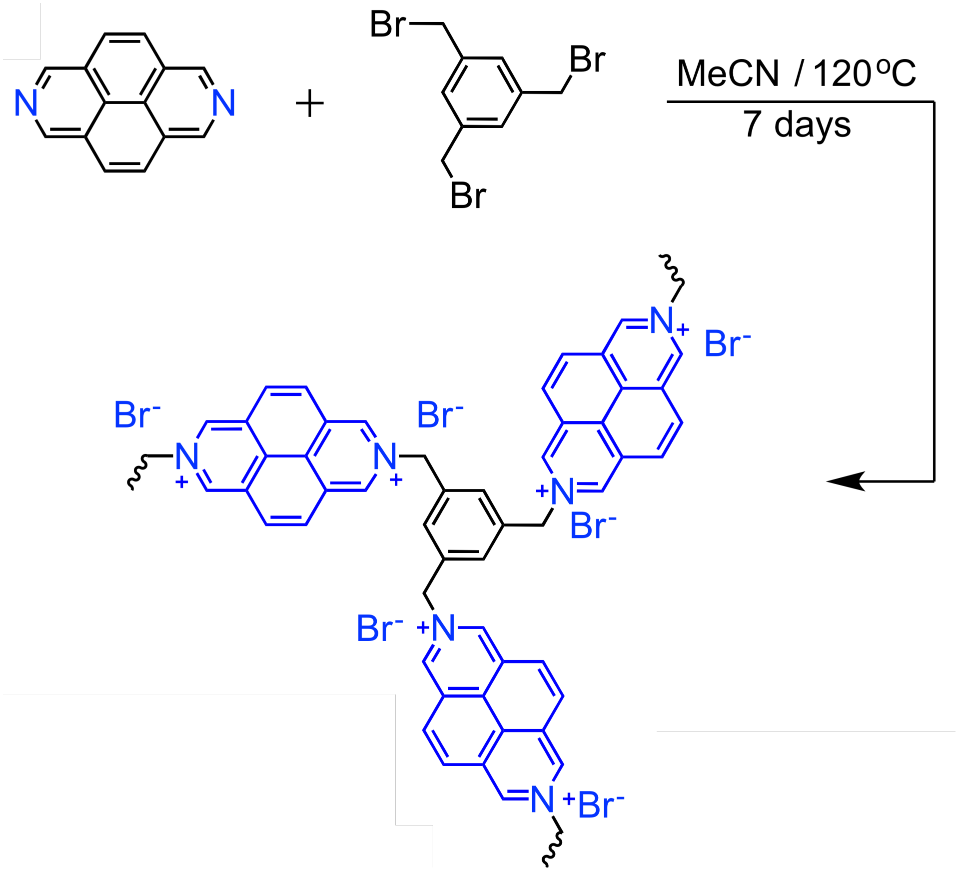
Methods of TGA and UV/Vis Analysis.

TGA: In order to probe the affinity of pDAP towards primary amines, thermogravimetric adsorption analysis was carried out by following weight increase upon exposure to the corresponsing amine vapor. The preactivation step was employed to remove moisture and trapped atmospheric gases by N_2 flow (50 mL min^{-1}) at 150℃ for 90 min. Then, pDAP was exposed to *n*-butylamine vapor by using N_2 as a carrier gas, which is bubbled through neat amine solution at a rate of 10 mL min^{-1} for 210 min at room temperature. The change of pDAP's weight was monitored during the analysis.

UV/Vis: The optical properties of pDAP were investigated in the presence of amine vapors. Three amines were chosen by their industrial relevance: *n*-butylamine (primary amine), diethylamine (secondary amine) and triethylamine (tertiary amine). Solid-state UV-Vis spectra were recorded by using Perkin Elmer-Lambda 1050S instrument (from 250 to 800 nm). For adsorption of aliphatic amines, 5 mL vial containing around 30 mg of pDAP was put into 100 mL vial filled with 20 mL related amines. The cap of large vial was closed to prevent amine vaporization. After exposure to each amine vapors for 30 min, the color change was observed from orange to dark green, which was easily observed by naked eye. For the demonstration of reversible adsorption / desorption of MEA in the solution phase, 20 mg of pDAP was dispersed using an ultrasonic bath in 9 mL of DI water in a 20 mL vial. Then, 1 mL MEA solution in H_2O (10 M) was added to this mixture to obtain 1 M MEA in the final mixture. The color of suspension was changed immediately from orange to dark green and the absorption change followed by using UV/Vis spectrometer. To regenerate the pDAP, 1M HCl was added to this mixture, which showed immediate recovery of original UV-Vis spectrum.

2. Synthesis

Synthesis of ***pDAP***



pDAP **:** 2,7-diazapyrene[1] (48 mg, 0.235mmol) and 1,3,5-bromomethyl benzene (56 mg, 0.156 mmol) were added into 100 mL Teflon Lined Hydrothermal Synthesis Autoclave Reactor and dissolved in MeCN (30mL). Then, the mixture was kept at 120°C for 7 days. After cooling it to room temperature, the resulting precipitate was filtered and extensively washed with acetonitrile (1 x 50 ml), $CHCl_3$ (3 x 50 mL), THF (3 x 50 mL) and diethyl ether (1 x 50 mL). The final solid was dried at room temperature under vacuum for 24 h to yield **pDAP** (92 mg, 90 %). ($C_{30}H_{21}Br_3N_3$) [found %, (calcd)] (CHN): 51.82 %C (54.33), 3.48 %H (3.19), 5.21 %N (6.34).

3. Characterization

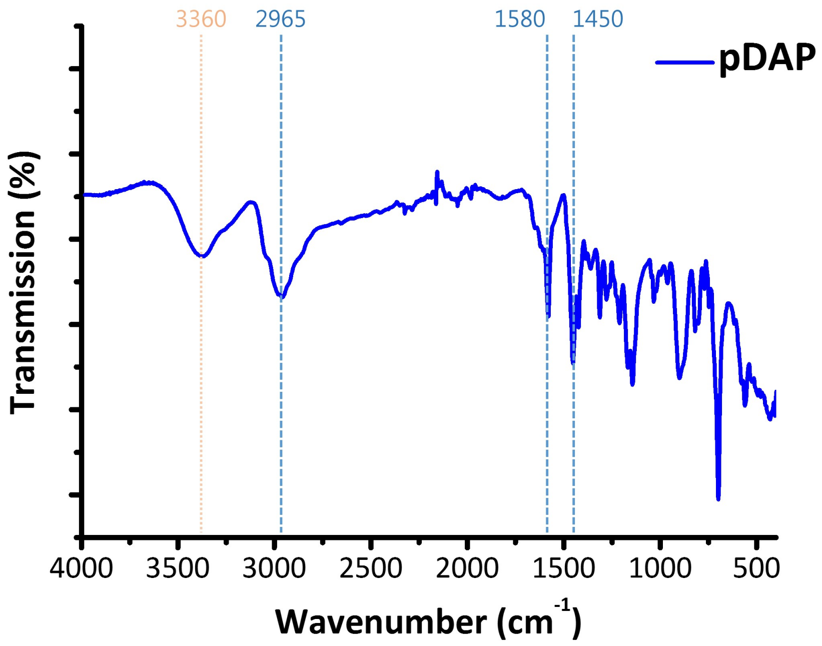


Figure S1. FT-IR spectrum of pDAP. The spectrum was recorded by using ATR mode under ambient conditions.

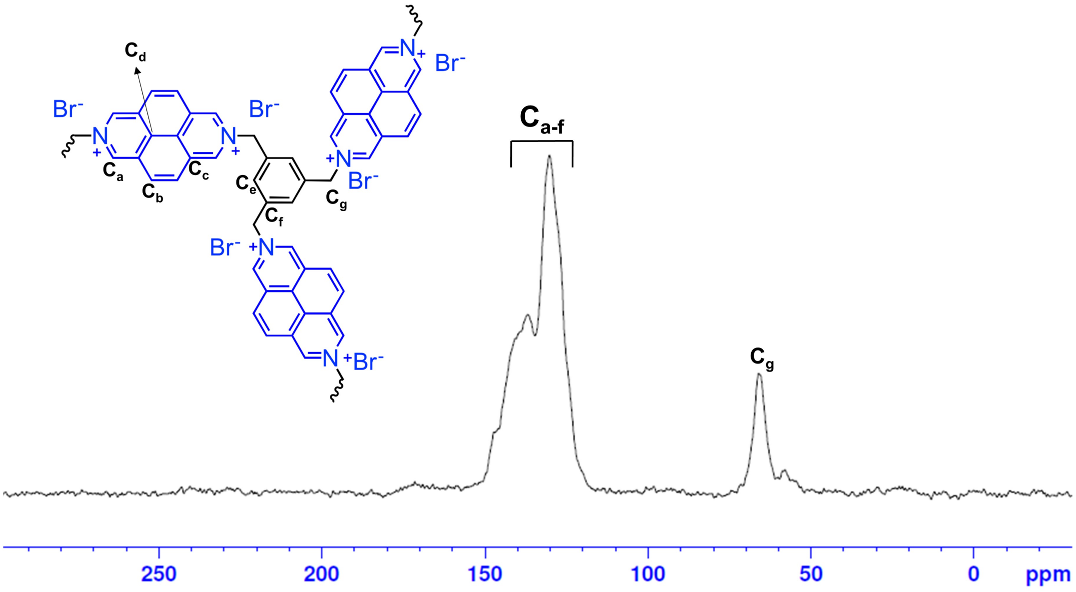


Figure S2. Solid state CP-MAS ^{13}C NMR spectrum of pDAP along with the corresponding peak assignments. The spectra were recorded with a contact time of 2 ms, a relaxation time of 5 s, and a spinning frequency of 7 kHz. Spinning side bands are omitted for clarity.

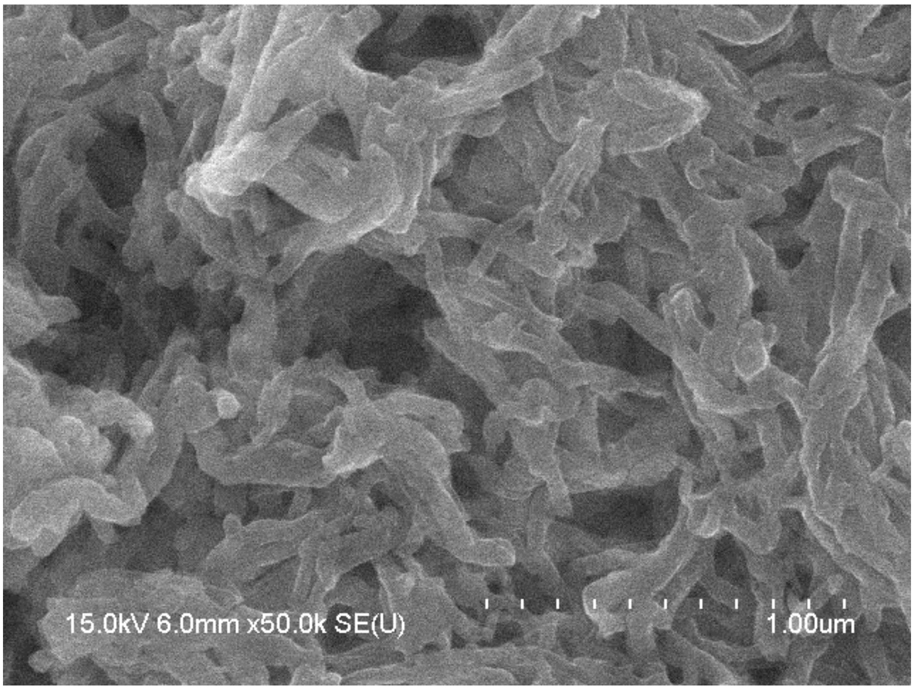
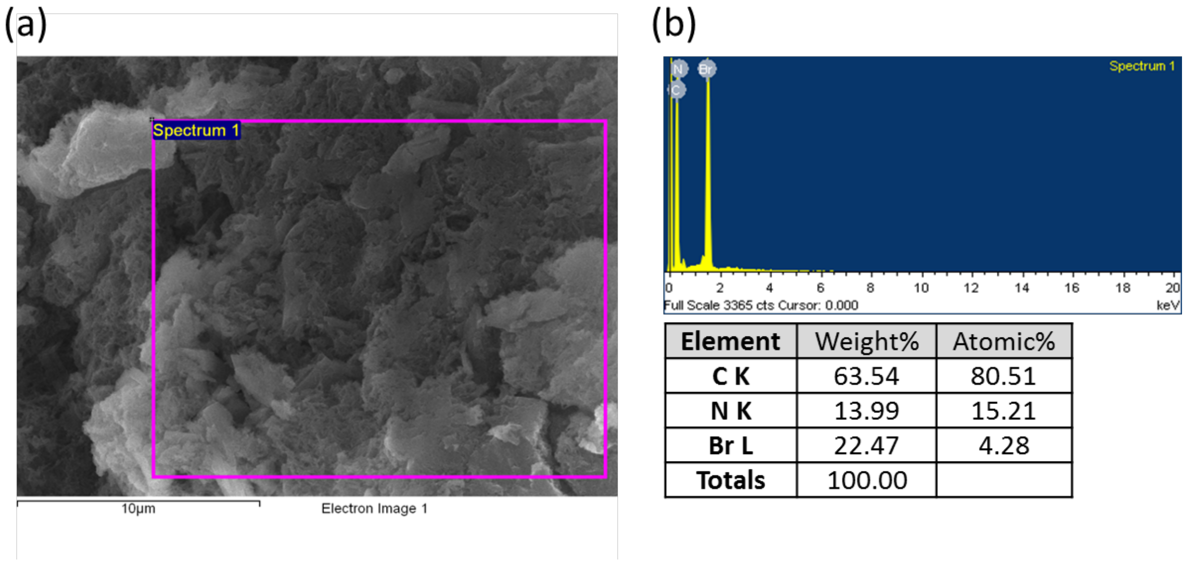


Figure S3. Scanning electron microscopy (SEM) image of pDAP.



Element	Weight%	Atomic%
C K	63.54	80.51
N K	13.99	15.21
Br L	22.47	4.28
Totals	100.00	

Figure S4. SEM image (a) and energy dispersive X-ray absorption spectroscopy (EDS) analysis of pDAP to probe carbon (C), nitrogen (N) and bromine (Br) atoms.

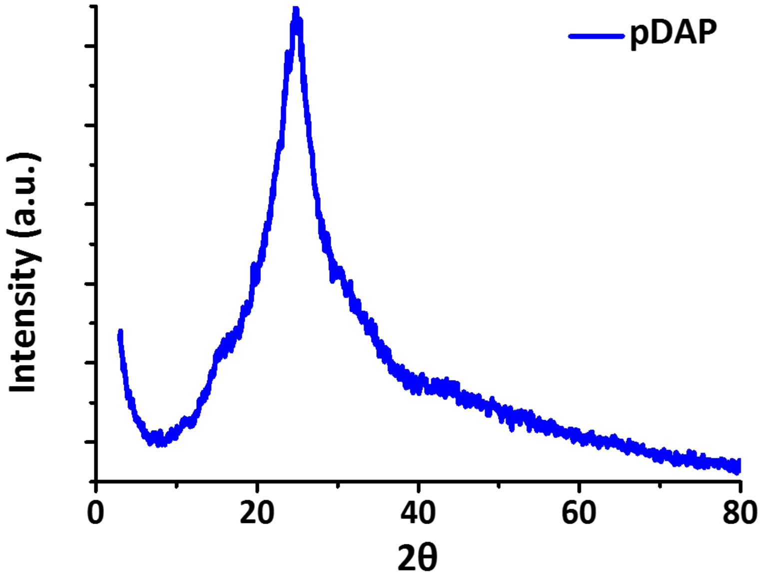


Figure S5. Powder X-ray diffraction pattern of pDAP, which shows the amorphous nature of pDAP.

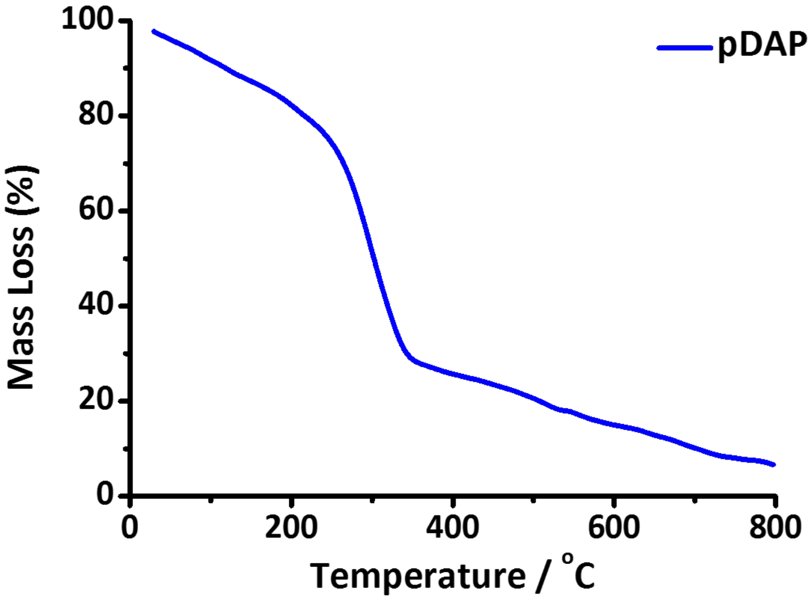


Figure S6. Thermogravimetric analysis of pDAP under N_2 atmosphere in the range from 30°C to 800°C at a rate of 10°C min^{-1}. The weight loss below 200°C was ascribed to the moisture.

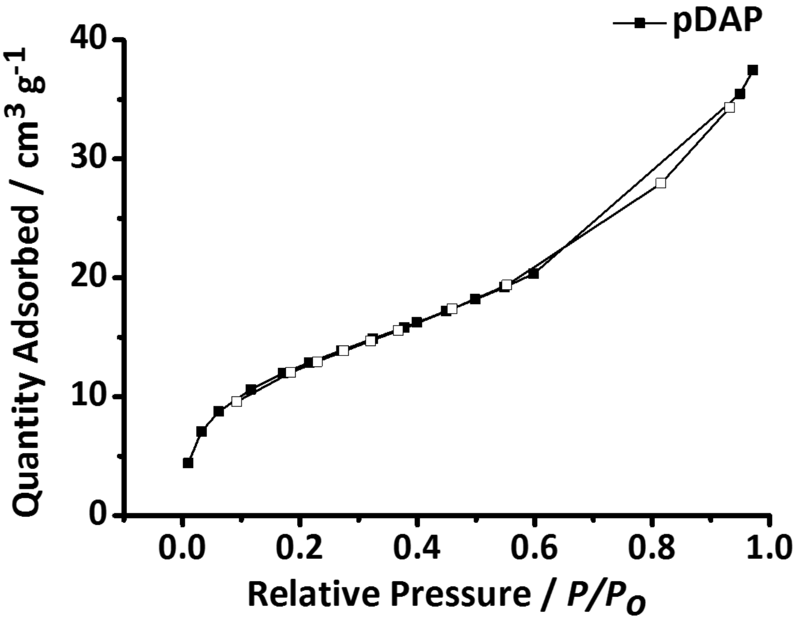


Figure S7. Argon adsorption/desorption isotherms of pDAP collected at 87 K. Filled and empty symbols represent adsorption and desorption, respectively.

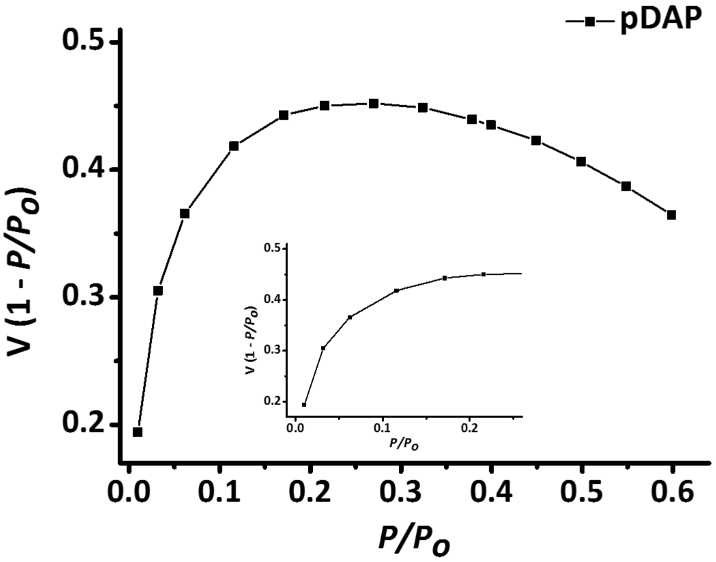
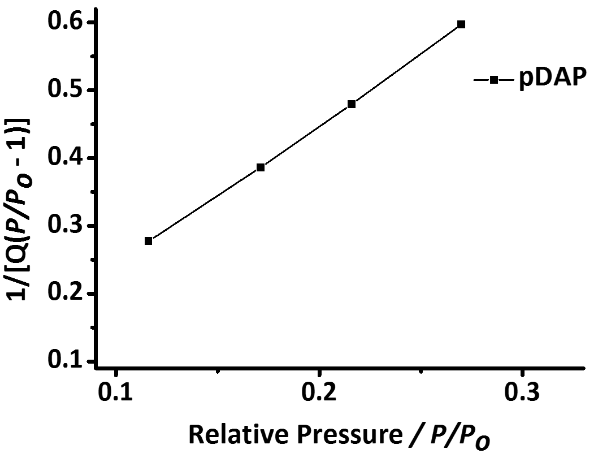


Figure S8. Calculated Rouquerol plots of pDAP (Inset: Enlarged plot turning part) along with pressure ranges used for BET surface area calculations. (Pressure Range from 0.01 to 0.25 (*P/P$_o$*))



$^{S}\text{BET}_{SA}$ (m^2g^{-1})	Equation	R^2
40.78	y = 2.08x+0.03	0.999

Figure S9. BET linear plot of pDAP from Ar isotherms at 87 K.

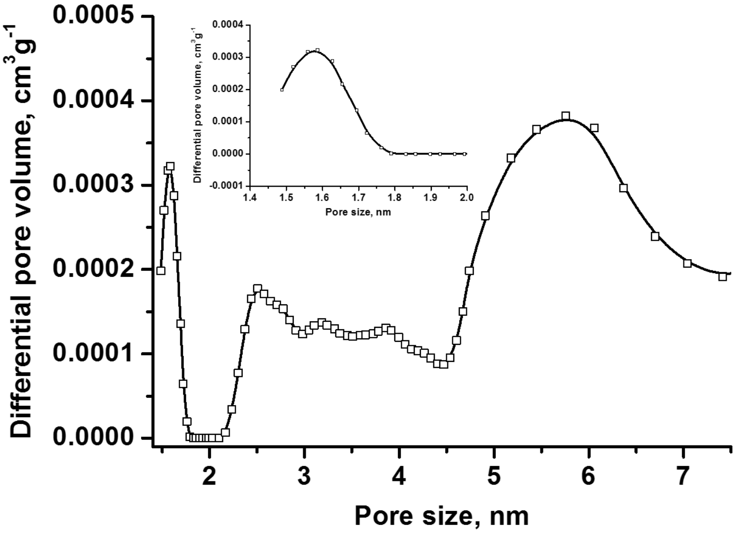


Figure S10. NLDFT pore size distribution of pDAP calculated Ar adsorption isotherms at 87 K. Inset: Micropore region of pDAP.

References

1 D. Cao, M. Juricek, Z. J. Brown, A. C. H. Sue, Z. C. Liu, J. Y. Lei, A. K. Blackburn, S. Grunder, A. A. Sarjeant, A. Coskun, C. Wang, O. K. Farha, J. T. Hupp and J. F. Stoddart, *Chem-Eur J*, 2013, **19**, 8457-8465.