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Electronic Supplementary Information (ESI)

Control of Porosity of Novel Carbazole-modified Polytriazine Frameworks for a High Selective Separation of CO_2/N_2

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1. The synthetic process



Scheme S1 the sythetic routes of monomers

3,6-Dibromo-9-methylcarbazole: 3,6-Dibromo-9H-carbazole (3.25 g, 10 mmol) and tetrabutyl ammonium bromide (322 mg, 1mmol) were dissolved in DMSO (50 mL), and then aqueous NaOH solution (50%, 2.55 mL) and iodomethane (0.93 mL, 15 mmol) were added. The mixture turned to orange and was stirred at 90 °C for 12 h. After cooling to room temperature the mixture was poured into water (200ml) and extracted with CH₂Cl₂. The organic layer was washed with water and dried with MgSO₄. Afterward, the solvent was removed by reduced pressure and the crude product was purified by silica column chromatography to give a white crystal (3.1 g, 91%).¹H NMR (400MHz, CDCl₃, ppm): $\delta = 8.13$ (S, 2 H), 7.58-7.55 (dd, J₁=8.0 Hz, J₂=4.0 Hz, 2 H), 7.27-7.25 (d, J=8.0 Hz, 2 H), 3.81 (s, 3H). GC-TOF/MS: m/z 339

3,6-Dicyano-9-methylcarbazole: 3,6-Dibromo-9-methylcarbazole (6.78 g, 20 mmol), cuprous cyanide (8.95 g, 100 mmol) and 18-Crown-6 (180 mg) were dissolved in dry DMF(100 mL) under N₂ atmosphere. After stirred for 48 h at 150 °C, the mixture was poured into a cold solution of 100 g of ferric chloride in 150 mL of concentrated hydrochloric acid for another 2 h. The brown solid was collected by filtration, washed with water and ethanol several times, and dried under vacuum. The crude product was purified by silica column chromatography to give a white solid (2.8 g, 60%).¹H NMR (300MHz, DMSO-d6, ppm): δ = 8.84 (S, 2 H), 7.98-7.95 (d, J=9.0 Hz, 2 H), 7.90-7.87 (d, J=9.0 Hz, 2 H), δ = 3.99 (S, 3 H). GC-TOF/MS: m/z 231

Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate: 3,6-Dibromo-9H-carbazole (3.25 g, 10 mmol), dry K₂CO₃ (3.73 g, 27 mmol) and tetrabutyl ammonium bromide (322 mg, 1mmol) were dissolved in dry DMF (50 mL), The mixture was stirred for 30min at 50 °C before ethyl bromoacetate (3.3 mL, 30 mmol) was added. The mixture was stirred at 90 °C for 12 h. After cooling to room temperature the mixture was poured into ice water (200ml) and extracted with CHCl₃. The organic layer was washed with water and dried with MgSO₄. Afterward, the solvent was removed by reduced pressure and the crude product was purified by silica column chromatography to give a white crystal (3.45 g, 84%). ¹H NMR (400MHz, CDCl₃, ppm): $\delta = 8.18$ (S, 2 H), 7.60-7.58 (d, J=8.0 Hz, 2 H), 7.24-7.23 (d, J=8.0 Hz, 2 H), 4.97 (S, 2 H), 4.24-4.20 (q, J=8.0 Hz, 2 H), 1.26-1.23 (t, J=4.0 Hz, 3 H)

Ethyl-2-(3,6-dicyano-9H-carbazol-9-yl)acetate: Ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate (8.22 g, 20 mmol), cuprous cyanide(8.95 g, 100 mmol) and 18-Crown-6 (180 mg) were dissolved in dry DMF(100 mL) under N_2 atmosphere. After stirred for 48 h at 150 °C, the mixture was poured into a cold solution of 100 g of ferric chloride in 150 mL of concentrated hydrochloric acid for another 2 h. The brown solid was collected by filtration, washed with water and ethanol several times, and dried under vacuum. The crude product was purified by silica column

chromatography to give a white solid (3.3 g, 55%).¹H NMR (500MHz, CDCl₃, ppm): δ = 8.45 (S, 2 H), 7.84-7.82 (d, J=10.0 Hz, 2 H), 7.45-7.48 (d, J=10.0 Hz, 2 H), 5.09 (S, 2 H), 4.29-4.25 (q, J=10.0 Hz, 2 H), 1.30-1.27 (t, J=5.0 Hz, 3 H)

3,6-Dibromo-9-phenylcarbazole: 3,6-Dibromo-9H-carbazole (3.25 g, 10 mmol), dry K₂CO₃ (3.73 g, 27 mmol), Copper powder (64 mg, 1 mmol), 1,10-Phenanthroline (180 mg, 1 mmol) were dissolved in dry DMF (50 mL). The mixture was stirred for 30min at 50 °C before iodobenzene (1.1 mL, 10 mmol) was added. The mixture was stirred for 48 h at 150 °C. After cooling to room temperature the mixture was poured into water (200ml) and extracted with CHCl₃. The organic layer was washed with water and dried with MgSO₄. Afterward, the solvent was removed by reduced pressure and the crude product was purified by silica column chromatography to give a white crystal (3.2 g, 80%).¹H NMR (500MHz, CDCl₃, ppm): $\delta = 8.19$ (s, 2H), 7.63-7.59 (t, J=10.0 Hz, 2H), 7.50 - 7.47 (m, 5H), 7.25-7.23 (d, J=10.0 Hz, 2H)

3,6-Dicyano-9-phenylcarbazole: 3,6-Dibromo-9-phenylcarbazole (7.92 g, 20 mmol), cuprous cyanide (8.95 g, 100 mmol) and 18-Crown-6 (180 mg) were dissolved in dry DMF (100 mL) under N₂ atmosphere. After stirred for 48 h at 150 °C, the mixture was poured into a cold solution of 100 g of ferric chloride in 150 mL of concentrated hydrochloric acid for another 2 h. The brown solid was collected by filtration, washed with water and ethanol several times, and dried under vacuum. The crude product was purified by silica column chromatography to give a white solid (2.9 g, 50%). ¹H NMR (300MHz, DMSO, ppm): $\delta = 8.92$ (s, 2H), 7.89-7.86 (d, J=15.0 Hz, 2H), 7.70-7.62 (m, 5H), 7.48-7.45(d, J=15.0 Hz, 2H)

NOP-19: NOP-19 was synthesized by heating a mixture of the 3,6-dicyano-9-methylcarbazole (1.0 g, 4.3 mmol) and ZnCl₂ (5.9 g, 43 mmol) in a quartz tube (3×10 cm). The tube was evacuated to a high vacuum and then sealed rapidly. Following by a temperature program (250° C/10h, 300° C/10h, 350° C/10h, 400° C/20h), the quartz tube was cooled to room temperature, and the reaction mixture was ground and then washed thoroughly with water to remove most of the catalyst. The crude product was stirred in diluted HCl for 15 h to remove the residual salt. The resulting black powder was filtered, and washed successively with water and methyl alcohol, followed by Soxhlet extraction overnight using acetone, methyl alcohol and hexane as eluting solvent sequentially, and dried in vacuum at 150 °C. Yield: 93%

NOP-20: NOP-20 was synthesized by heating a mixture of the ethyl-2-(3,6-dicyano-9H-carbazol-9-yl)acetate (1.0 g, 3.3 mmol) and ZnCl₂ (4.5 g, 33 mmol) in a quartz tube (3×10 cm). The tube was evacuated to a high vacuum and then sealed rapidly. Following by a temperature program (250° C/10h, 300° C/10h, 350° C/10h, 400° C/20h), the quartz tube was cooled to room temperature, and the reaction mixture was ground and then washed thoroughly with water to remove most of the catalyst. The crude product was stirred in the boiled water for 15h twice to remove the residual salt. The resulting black powder was filtered, and washed successively with water and methyl alcohol, followed by Soxhlet extraction overnight using acetone, methyl alcohol and hexane as eluting solvent sequentially, and dried in vacuum at 150 °C. Yield: 90%

NOP-21: NOP-21 was synthesized by heating a mixture of the 3,6-dicyano-9-phenylcarbazole (1.0 g, 3.4 mmol) and ZnCl₂ (4.6 g, 34 mmol) in a quartz tube (3×10 cm). The tube was evacuated to a high vacuum and then sealed rapidly. Following by a temperature program (250° C/10h, 300° C/10h, 350° C/10h, 400° C/20h), the quartz tube was cooled to room temperature, and the reaction mixture was ground and then washed thoroughly with water to remove most of the catalyst. The crude product was stirred in diluted HCl for 15 h to remove the residual salt. The resulting black powder was filtered, and washed successively with water and methyl alcohol, followed by Soxhlet extraction overnight using acetone, methyl alcohol and hexane as eluting solvent sequentially, and dried in vacuum at 150 °C. Yield: 94%

2. Materials and Method

3,6-Dibromo-9H-carbazole, iodomethane, ethyl bromoacetate, iodobenzene and Copper(I) cyanide

was purchased from Alfa Aesar Chemical Inc. and used as received. 1,10-Phenanthroline, 18crown-6, tetrabutyl ammonium bromide, Copper(I)iodide, copper powder was purchased from Aladdin Chemical Inc. and used as received. ZnCl₂ was refluxed over SOCl₂ and filtered just before use. Unless otherwise specified, all other solvents and reagents were purchased from Energy Inc. and used as received.

Fourier transform infrared spectroscopy (FTIR) was collected with a VARIAN 1000 FTIR (scimitar series) spectrometer in the 400-4000 cm⁻¹ region. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. NMR data were collected on a Bruker 400MHz spectrometer at 25°C, using tetramethylsilane as an internal reference. For scanning electron microscopy imaging (SEM), samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then coated with gold at a pressure of 1×10^{-5} mbar under a nitrogen atmosphere for 90 seconds before imaging. Images were taken on a Quanta-200 Scanning Electron Microscope. High-resolution Transmission electron microscopy (HRTEM) was performed on a Phillips CM 200 FEG electron micro-scope equipped with a field emission gun. Powder X-ray diffraction data were collected on a Panalytical X'pert pro multipurpose diffractometer. Samples were mounted on a sample holder and measured using Cu Ka radiation with a theta range of 5-80. Thermo-gravimetric analysis (TGA) was performed at a heating rate of 10K/min under air atmosphere using a PERKIN ELMER TGA7. The gas adsorption-desorption isotherms were performed on a Micromeritics ASAP 2020 analyzer. N₂ adsorption – desorption measurements were carried out at 77 and 273 K, CO₂ adsorption – desorption isotherms were collected at 273 and 298 K, respectively. High purity gas (99.999 %) was used for the adsorption experiments. Prior to measurements, the samples were degassed at 200°C under high vacuum for 12 h. Liquid nitrogen bath and an ice-water bath equipped with a temperature sensor were utilized to control the temperature at 77, 273, and 298K, respectively. The apparent surfaces areas (BET) for N2 were calculated using the Brunauer-Emmett-Teller (BET) model range from 0.01 to 0.1 bar for three samples. Microporous volumes were calculated using single-point measurements at $P/P_0 = 0.1$, while the total porous volumes were obtained at $P/P_0 = 0.9$. Pore size distributions were derived from the N₂ adsorption isotherms using the Non-local density functional theory (NLDFT).

3. Infrared spectroscopy



Fig.S1 Infrared spectra of monomers







Fig.S3 Infrared spectra of NOP-20 and the corresponding monomer (the top one)

4.¹H NMR



Fig.S4 ¹H NMR spectrum of 3,6-dibromo-9-methylcarbazole



Fig.S5 ¹H NMR spectrum of 3,6-dicyano-9-methylcarbazole



Fig.S6 ¹H NMR spectrum of ethyl-2-(3,6-dibromo-9H-carbazol-9-yl)acetate



Fig.S7 ¹H NMR spectrum of ethyl-2-(3,6-dicyano-9H-carbazol-9-yl)acetate



Fig.S8 ¹H NMR spectrum of 3,6-dibromo-9-phenylcarbazole



Fig.S9 ¹H NMR spectrum of 3,6-dicyano-9-phenylcarbazole

5. Elemental analysis

	Found (%) ^{a,b}			Calculated (%)		
	С	Ν	Н	С	Ν	Н
NOP-19	76.21	9.32	4.55	77.91	18.17	3.92
NOP-20	70.26	7.25	4.37	71.28	13.85	4.32
NOP-21	78.79	8.36	3.89	81.89	14.33	3.78

Tab.S1 Elemental analysis data of the polymers

a) For NOP-19,20,21, the carbonization can attributed to the decomposition of a small amount aromatic nitrile monomers sublimating away from the reaction system;

b) The deviations between the residual weight by EA and the calculated weight from total mass maybe caused by incomplete combustion of the samples similar to literature.

Elemental analysis gives a much lower nitrogen content and concomitantly a much higher C/N ratio than the theoretically calculated values. This indicates that the part of the nitrogen is lost to decomposition. Thus, a significant amount of nitriles cleavage of the weakest Ar-CN bonds has to be taken into account.

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Scheme S2 General schematic representation for the decomposition of a triazine ring

6. Thermogravimetric analysis



Fig.S10 TGA of the NOPs under air condition (Residual mass at 800 °C is 4.9 wt%, 4.3 wt%, 6.7 wt% for NOP-19,20,21 under air atmosphere)

7. Morphology analysis by SEM and TEM



Fig.S11 Scanning electron micrographs of NOP-19



Fig.S12 Scanning electron micrographs of NOP-20



Fig.S13 Scanning electron micrographs of NOP-21



Fig.S14 TEM micrograph of NOP-19



Fig.S15 TEM micrograph of NOP-20



Fig.S16 TEM micrograph of NOP-21

8. XRD analysis



Fig.S17 PXRD pattern of NOP-19



Fig.S18 PXRD pattern of NOP-20



Fig.S19 PXRD pattern of NOP-21

9. Gas adsorption selectivity study



Fig.S20 CO₂ (red circles) and N₂ (black squares) uptakes of NOP-19 at 273K. Isotherms were fitted to a dual-site Langmuir equation



Fig.S21 CO₂ (red circles) and N₂ (black squares) uptakes of NOP-20 at 273K. Isotherms were fitted to a dual-site Langmuir equation



Fig.S22 CO₂ (red circles) and N₂ (black squares) uptakes of NOP-21 at 273K. Isotherms were fitted to a dual-site Langmuir equation



Fig.S23 CO_2 (red circles) and N_2 (black squares) uptakes of NOP-19 at 273K



Fig.S24 CO_2 (red circles) and N_2 (black squares) uptakes of NOP-20 at 273K



Fig.S25 CO_2 (red circles) and N_2 (black squares) uptakes of NOP-21 at 273K



Fig.S26 Initial slope selectivity study of NOP-19 at 273K (CO₂ over N₂)



Fig.S27 Initial slope selectivity study of NOP-20 at 273K (CO_2 over N_2)



Fig.S28 Initial slope selectivity study of NOP-21 at 273K (CO₂ over N₂)

10. ¹³C NMR



Fig.S29 Solid ¹³C NMR spectrum of NOP-19