Supporting Information for

Tunable Porosity of nanoporous organic polymers with

hierarchical pores for enhanced CO₂ capture †

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Table of Contents

1. Synthesis of NOPs	.2
2. FTIR spectra of the NOPs	.3
3. The ¹³ C CP/MAS NMR spectrum of NOPs	.4
4. Elemental analysis	.4
5. Powder X-ray diffraction patterns of NOPs	.5
6. SEM and TEM image of NOP-50A	.5
7. TGA curves for NOPs	.6

1. Synthesis of NOPs

Synthesis of NOP-50B: Carbazole (0.3344 g, 2 mmol) and BCMBP(3.012 g, 12 mmol) and FeCl₃ (2.2692 g, 14 mmol) was added to a dry 100 mL three-necked round-bottom flask equipped with a condenser and a mechanical agitation device. 20 mL anhydrous 1, 2-dichloroethane was injected into the aforementioned mixture under a flow of nitrogen. The mixture was heated to 80 °C for 24 h under a nitrogen atmosphere at constant stirring. After cooling to room temperature, the precipitate was collected by filtration and washed with methanol until the filtrate turned clear. Further purification of the polymer was carried out by Soxhlet extraction with methanol and chloroform, and dried in vacuum at 80 °C for 24 h. NOP-50B was obtained in a yield of 96 % as a brownish-green colored, powdery solid.

Synthesis of NOP-51A: Ferrocene (0.372 g, 2 mmol) and DCX(2.100 g, 12 mmol) and FeCl₃ (2.2692 g, 14 mmol) was added to a dry 100 mL three-necked round-bottom flask equipped with a condenser and a mechanical agitation device. 20 mL anhydrous 1, 2-dichloroethane was injected into the aforementioned mixture under a flow of nitrogen. The mixture was heated to 80 °C for 24 h under a nitrogen atmosphere at constant stirring. After cooling to room temperature, the precipitate was collected by filtration and washed with methanol until the filtrate turned clear. Further purification of the polymer was carried out by Soxhlet extraction with methanol and chloroform, and dried in vacuum at 80 °C for 24 h. NOP-51A was obtained in a yield of 97 % as a brownness colored, powdery solid.

Synthesis of NOP-51B: Ferrocene (0.372 g, 2 mmol) and BCMBP(3.012 g, 12 mmol) and FeCl₃ (2.2692 g, 14 mmol) was added to a dry 100 mL three-necked round-bottom flask equipped with a condenser and a mechanical agitation device. 20 mL anhydrous 1, 2-dichloroethane was injected into the aforementioned mixture under a flow of nitrogen. The mixture was heated to 80 °C for 24 h under a nitrogen atmosphere at constant stirring. After cooling to room temperature, the precipitate was collected by filtration and washed with methanol until the filtrate turned clear. Further purification of the polymer was carried out by Soxhlet extraction with methanol and chloroform, and dried in vacuum at 80 °C for 24 h. NOP-51B was obtained in a yield of 98 % as a brownness colored, powdery solid.

Synthesis of NOP-52A: Triptycene (0.5087 g, 2 mmol) and DCX(2.100 g, 12 mmol) and FeCl₃ (2.2692 g, 14 mmol) was added to a dry 100 mL three-necked round-bottom flask equipped with a condenser and a mechanical agitation device. 20 mL anhydrous 1, 2-dichloroethane was injected into the aforementioned mixture under a flow of nitrogen. The mixture was heated to 80 °C for 24 h under a nitrogen atmosphere at constant stirring. After cooling to room temperature, the precipitate was collected by filtration and washed with methanol until the filtrate turned clear. Further purification of the polymer was carried out by Soxhlet extraction with methanol and chloroform, and dried in vacuum at 80 °C for 24 h. NOP-51B was obtained in a yield of 99 % as a brownness colored, powdery solid.

Synthesis of NOP-52B: Triptycene (0.5087 g, 2 mmol) and BCMBP(3.012 g, 12 mmol) and FeCl₃ (2.2692 g, 14 mmol) was added to a dry 100 mL three-necked round-bottom flask equipped with a condenser and a mechanical agitation device. 20 mL anhydrous 1, 2-dichloroethane was injected into the aforementioned mixture under a flow of nitrogen. The mixture was heated to 80 °C for 24 h under a nitrogen atmosphere at constant stirring. After cooling to room temperature, the precipitate was collected by filtration and washed with methanol until the filtrate turned clear. Further purification of the polymer was carried out by Soxhlet extraction with methanol and chloroform, and dried in vacuum at 80 °C for 24 h. NOP-52B was obtained in a yield of 95 % as a brownness colored, powdery solid.



2. FTIR spectra of the NOPs

Fig S1. FTIR spectra of the NOPs.

3. The ¹³C CP/MAS NMR spectrum of NOPs



Fig S2. ¹³C CP/MAS NMR spectrum of NOPs

4. Elemental analysis

Tab ST. Elemental analysis data of the polymers						
Polymers	C (%)	N (%)	Fe (%)	Cl (%)		
NOP-50A	96.35	1.00		2.66		
NOP-51A	98.24	/	0.39	1.36		
NOP-52A	98.74	/	/	1.26		
NOP-50B	98.2	0.57	/	1.22		
NOP-51B	97.05	/	0.16	2.78		
NOP-52B	96.07	/	/	3.93		

Tab S1. Elemental analysis data of the polymers

5. Powder X-ray diffraction patterns of NOPs



Fig S3. PXRD spectra of NOP-50A and NOP-50B.

6. SEM and TEM image of NOP-50A



Fig S4.SEM image (a) and TEM image (b) of NOP-50A

7. TGA curves for NOPs



Fig S5.TGA plots of NOP-50, NOP-51 and NOP-52.