

Supporting Information

Aromatic-Rich Hydrocarbon Porous Networks through Alkyne Metathesis

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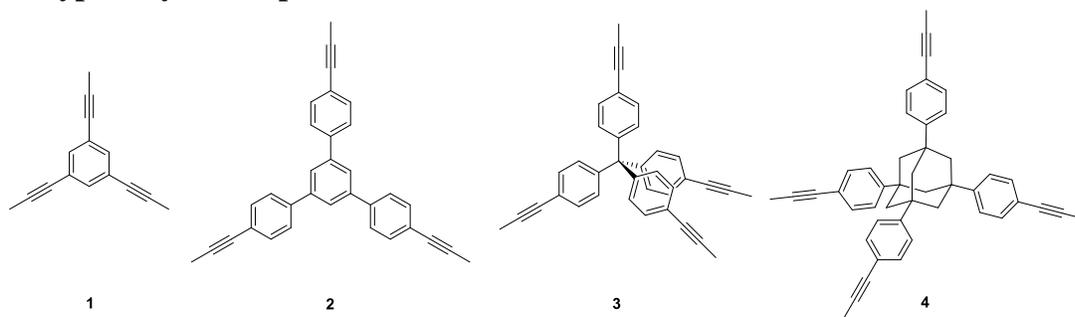
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1. Typical synthetic procedure of the monomers 1-4



Synthesis of 1,3,5-Tripropynylbenzene (1)

To a solution of anhydrous zinc bromide (3.10 g, 13.77 mmol) in THF (12 mL) was added 1-propynyl lithium (0.69 g, 15.0 mmol) dropwise at rt, followed by Pd(PPh₃)₄ (0.66 g, 0.57 mmol) and 1,3,5-tribromobenzene (0.95 g, 3.00 mmol). The reaction mixture was heated at 80 °C overnight, and was cooled to room temperature. The reaction was quenched with saturated aqueous solution of ammonium chloride and dichloromethane (100 mL) was added. The organic layer was washed successively with water (50 mL) and brine (50 mL) and then dried over anhydrous MgSO₄. The volatiles were evaporated and the residue was purified through flash column chromatography (hexane/ether 50/1) to afford **1** (0.42 g, 73%): ¹H NMR (500 MHz, CDCl₃) δ 7.28 (s, 3H), 2.02 (s, 12H). The ¹H NMR data is consistent with the literature report.¹

*Synthesis of 1,3,5-tris(*p*-propynylphenyl)benzene (2)*

The procedure of Negishi-coupling reaction described for the preparation of **1** was followed. 1,3,5-tris(*p*-propynylphenyl)benzene (**2**) (0.57 g, 82%) was obtained from 1,3,5-tris(*p*-bromophenyl)benzene (0.90 g, 1.66 mmol), propynyl lithium (0.38 g, 8.26 mmol), ZnBr₂ (1.70 g, 7.55 mmol), and Pd(PPh₃)₄ (0.36 g, 0.31 mmol). The physical data of **2**: ¹H NMR (300 MHz, CDCl₃) δ 7.73 (s, 3H), 7.65 – 7.55 (m, 6H), 7.54 – 7.45 (m, 6H), 2.09 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 141.7, 139.9, 132.0, 127.1, 124.9, 123.4, 86.8, 79.5, 4.4. HRMS (ESI): calcd. for C₃₃H₂₄⁺ [M⁺]: 420.1878. Found: 420.1873.

Synthesis of Tetrakis(p-propynylphenyl)methane (3)

The procedure of Negishi-coupling reaction described for the preparation of **1** was followed.

Tetrakis(*p*-propynylphenyl)methane (**3**) (0.61 g, 82%) was obtained from tetrakis(*p*-bromophenyl)methane (1.0 g, 1.57 mmol), propynyl lithium (0.47 g, 10.22 mmol), ZnBr₂ (2.10 g, 9.33 mmol), and Pd(PPh₃)₄ (0.45 g, 0.39 mmol). The physical data of **3**: ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, 8H, *J* = 8.5 Hz), 7.05 (d, 8H, *J* = 8.5 Hz), 2.04 (s, 12H). The ¹H NMR data is consistent with the literature report.²

Synthesis of 1,3,5,7-Tetrakis(p-propynylphenyl)adamantane (4)

The procedure of Negishi-coupling reaction described for the preparation of **1** was followed. 1,3,5,7-Tetrakis(*p*-propynylphenyl)adamantane (**4**) (0.20 g, 25%) was obtained from 1,3,5,7-tetrakis(*p*-bromophenyl)adamantane (1.02 g, 1.36 mmol), propynyl lithium (0.44 g, 0.37 mmol), and ZnBr₂ (1.96 g, 8.7 mmol), and Pd(PPh₃)₄ (0.43 g, 0.37 mmol). The physical data of **4**: ¹H NMR (300 MHz, CDCl₃) δ 7.37 (s, 16H), 2.09 (s, 12H), 2.04 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 148.5, 131.5, 124.9, 121.8, 85.5, 79.5, 46.8, 39.2, 4.3. HRMS (ESI): calcd. for C₉₂H₈₀Li⁺ [2M+Li⁺]: 1191.6415. Found: 1191.6378.

2. Typical synthetic procedure of PAE series

Typical synthetic procedure described for the preparation porous poly(aryleneethynylene) networks through alkyne metathesis was followed.² The triphenolsilane (5.1 mg, 0.01 mmol) and molybdenum(VI) trisamide precursor (8.3 mg, 0.01 mmol) were premixed in dry CCl₄ (1.3 mL) for 15 minutes at rt to generate the catalyst *in situ*. Subsequently, a solution of 1,3,5-tris(*p*-propynylphenyl)benzene (**2**) (116.9 mg, 0.28 mmol) in CHCl₃ (5.1 mL) was added followed by 5 Å molecular sieves (1.26 g, pellet, 8 – 12 mesh). The reaction was heated at 55 °C for 22 h without stirring. Acetone (~ 100 mL) was added, and the gel like network was broken into tiny pieces. The suspension was separated from the molecular sieves by decantation. The acetone suspension was centrifuged and most of the solvent was removed. The resultant mixture was poured into conc. ammonium hydroxide (100 mL) with vigorous stirring. The yellow solid was collected by filtration, washed with water (2 x 30 mL), and dried under high vacuum overnight to yield the network (87 mg, 92%). Elemental analysis for **PAE 2-2**: (C₂₇H₁₅)_n Calcd. C, 95.55%; H, 4.45%. Found. C, 83.36%; H, 4.60%.

Following similar procedure, **PAE 1-1** was obtained as a white solid (38 mg, 82%) from the monomer **1** (80 mg, 0.42 mmol) following the similar procedure. Elemental analysis for **PAE 1-1**: $(C_9H_3)_n$ Calcd. C, 97.28%; H, 2.72%. Found. C, 76.52%; H, 3.16%; **PAE 1-2** was obtained as a white solid (73 mg, quantitative) from monomer **1** (31 mg, 0.16 mmol) and **2** (68 mg, 0.16 mmol) following the similar procedure. Elemental analysis for **PAE 1-2**: $(C_{36}H_{18})_n$ Calcd. C, 95.97%; H, 4.03%. Found. C, 84.22%; H, 3.81%; **PAE 2-3** was obtained as a white solid (121 mg, quantitative) from monomer **2** (84 mg, 0.20 mmol) and **3** (71 mg, 0.15 mmol) following the similar procedure. Elemental analysis for **PAE 2-3**: $(C_{64}H_{35.53})_n$ Calcd. C, 95.55%; H, 4.45%. Found. C, 86.83%; H, 4.32%; **PAE 1-3** was obtained as a white solid (102 mg, quantitative) from the monomer **1** (51 mg, 0.27 mmol) and **3** (94 mg, 0.2 mmol) following the similar procedure. Elemental analysis for **PAE 1-3**: $(C_{40.7}H_{19.9})_n$ Calcd. C, 96.06%; H, 3.94%; Found. C 77.31%; H, 3.70%; **PAE 4-4** was obtained as a white solid (99 mg, quantitative) from the monomer **4** (120 mg, 0.20 mmol) following the similar procedure. Elemental analysis for **PAE 4-4**: $(C_{18}H_{28})_n$ Calcd. C, 88.45%; H, 11.55%. Found. C, 80.51%; H, 3.79%.

3. Thermal gravimetric analysis of PAE series

Samples were run on a TA Instruments Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere. A 10 K min^{-1} ramp rate was used. The materials show a good thermal stability up to at least 400 °C.

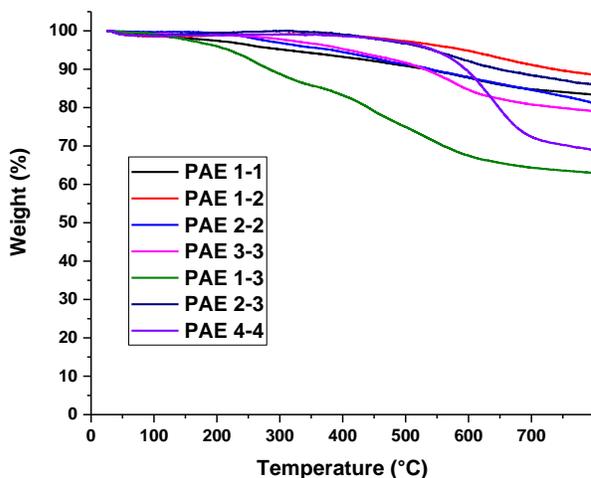


Figure S1. TGA of PAE series

4. FT-IR spectra of starting materials and PAE series

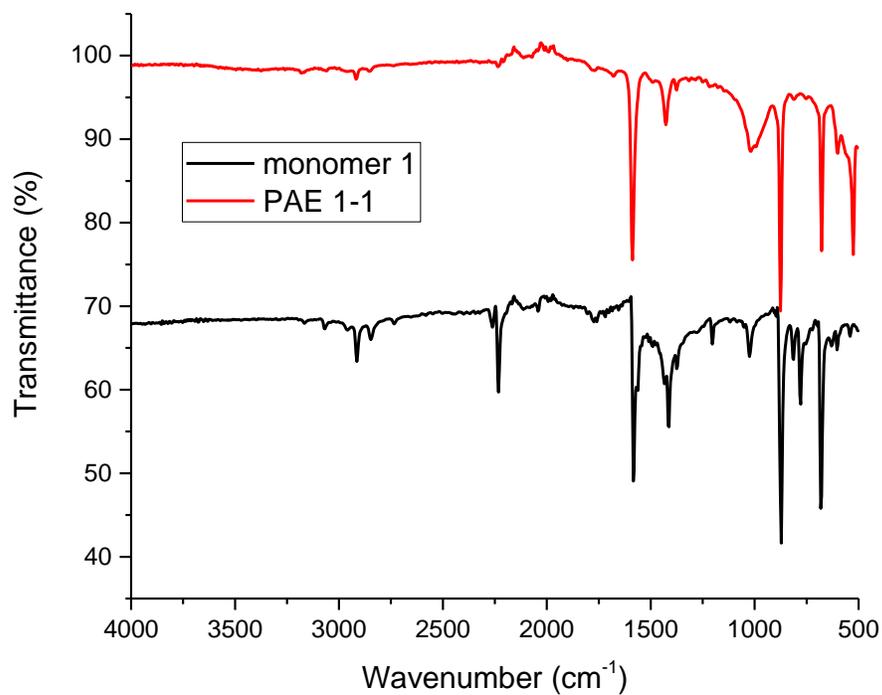


Figure S2. FT-IR spectra of monomer **1** and as synthesized **PAE 1-1**.

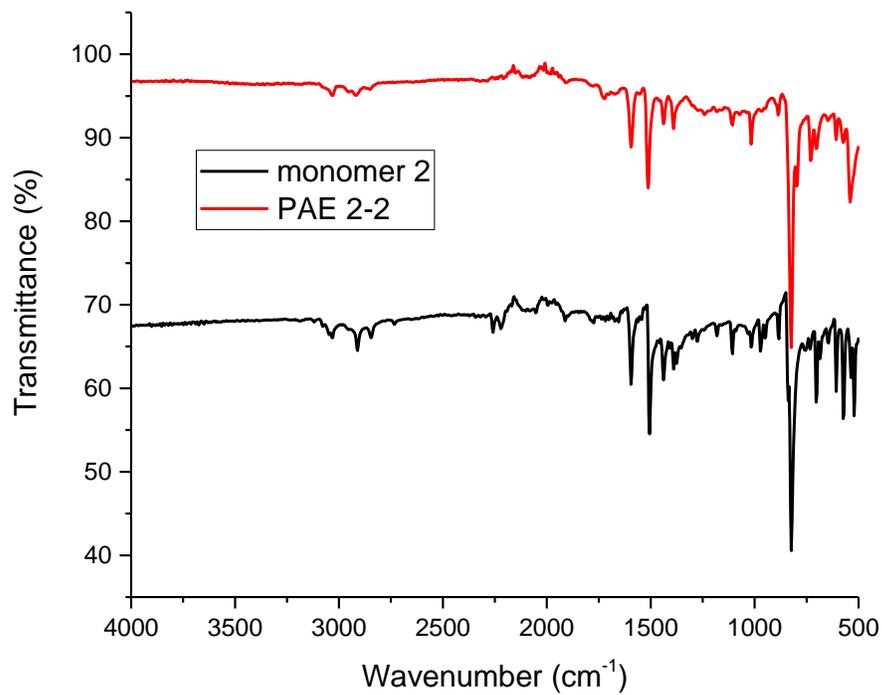


Figure S3. FT-IR spectra of monomer **2** and as synthesized **PAE 2-2**.

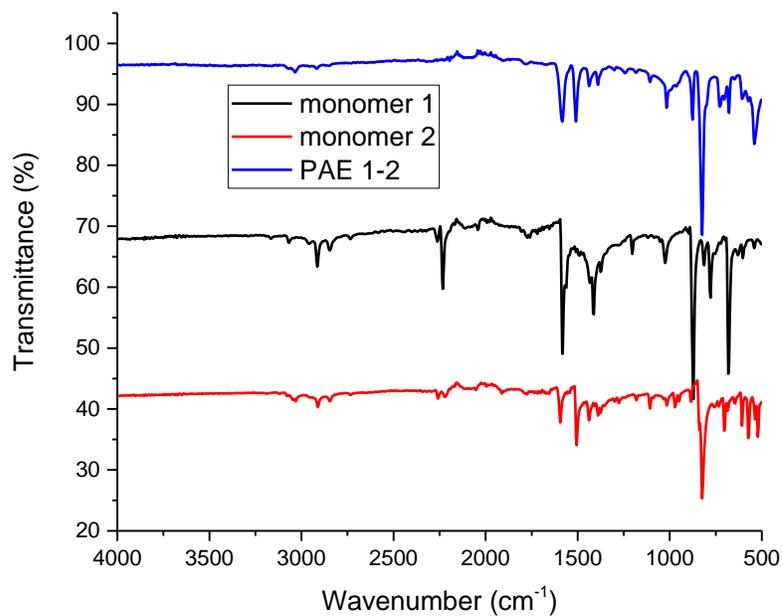


Figure S4. FT-IR spectra of monomers **1** and **2** and as synthesized **PAE 1-2**.

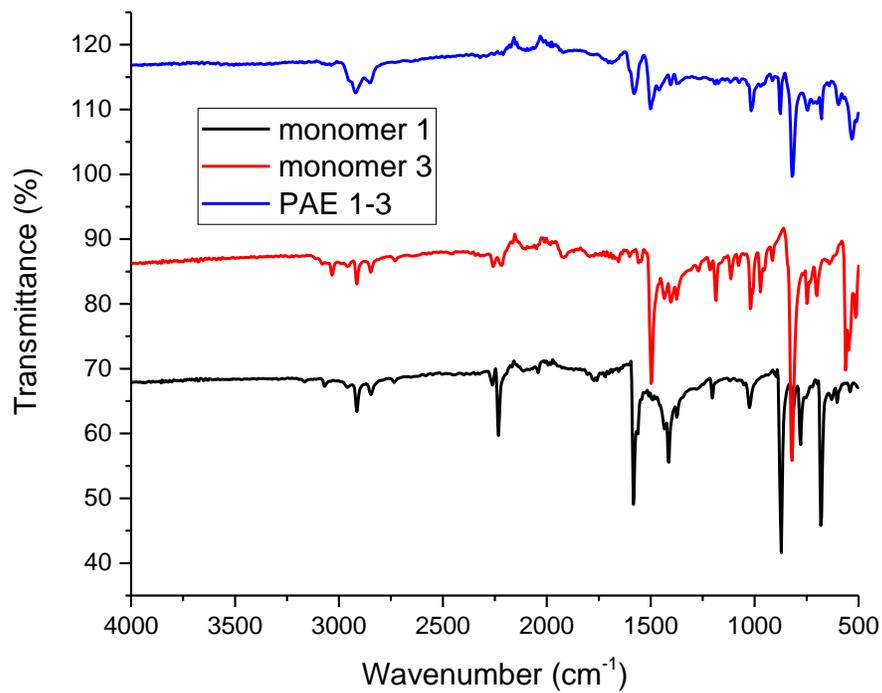


Figure S5. FT-IR spectra of monomers **1** and **3** and as synthesized **PAE 1-3**.

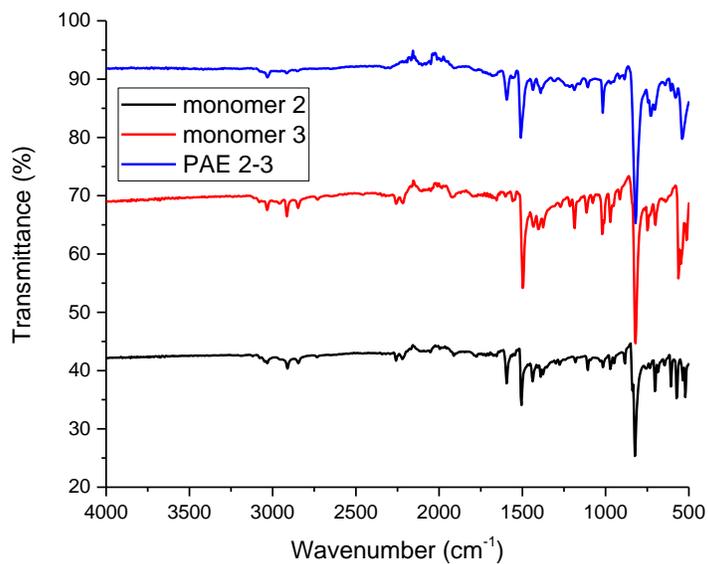


Figure S6. FT-IR spectra of monomers **2** and **3** and as synthesized **PAE 2-3**.

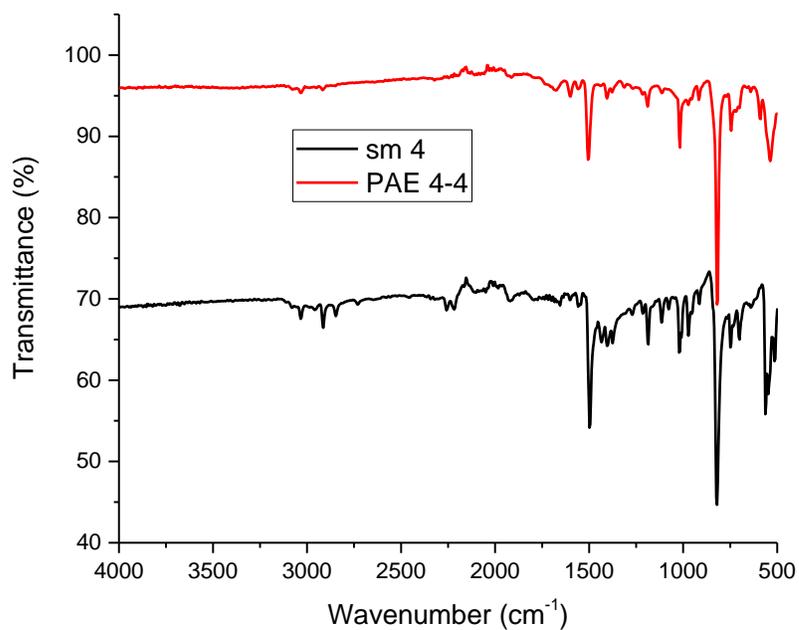


Figure S7. FT-IR spectra of monomer **3** and as synthesized **PAE 3-3**.

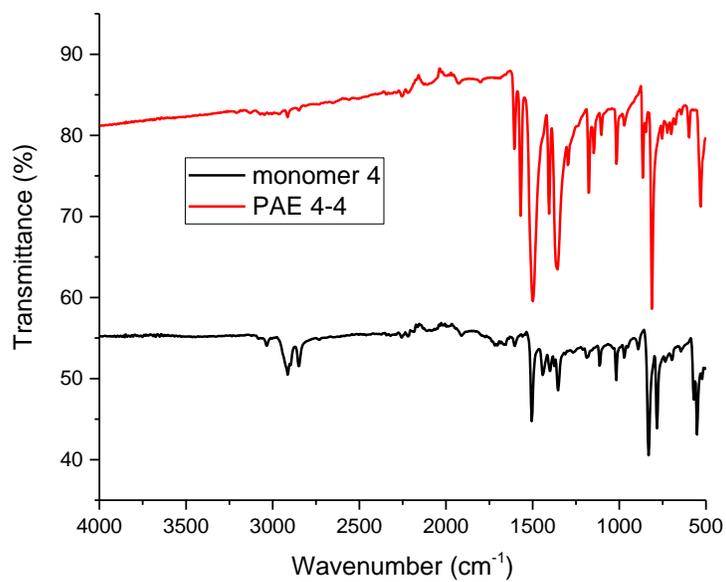


Figure S8. FT-IR spectra of monomer **4** and as synthesized **PAE 4-4**.

5. Powder X-Ray Diffraction of PAE 2-2

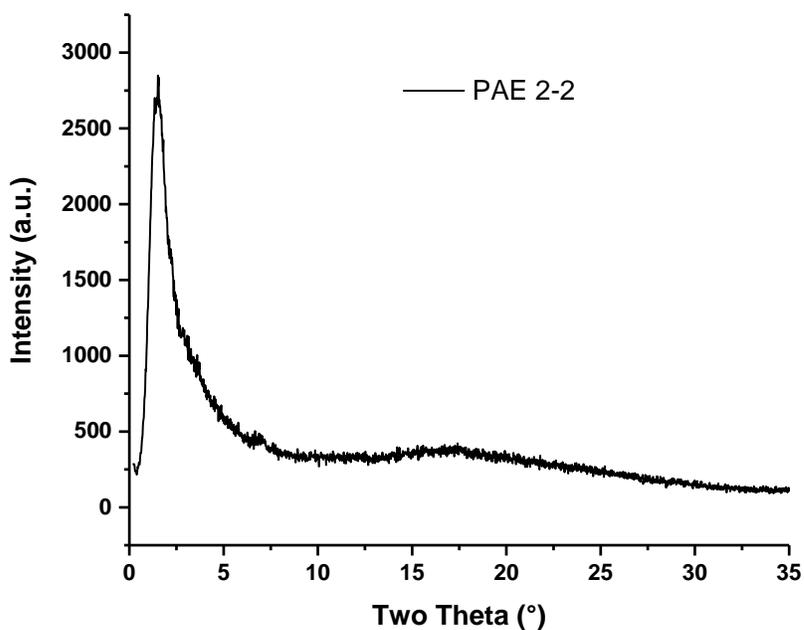


Figure S9. Powder X-ray diffraction of PAE 2-2.

6. N₂ adsorption (filled symbol) and desorption (open symbol) isotherms PAE series

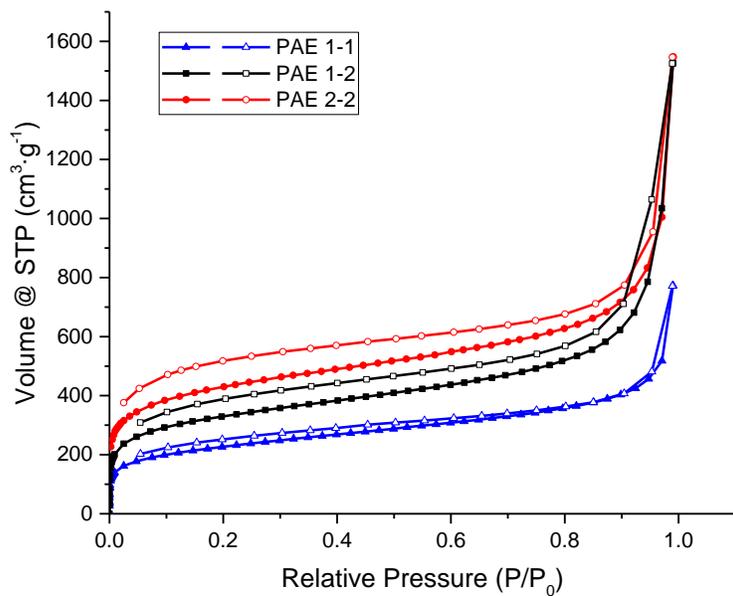


Figure S10. N₂ adsorption (filled symbol) and desorption (open symbol) isotherms for PAE series containing planar monomers **1** and **2**.

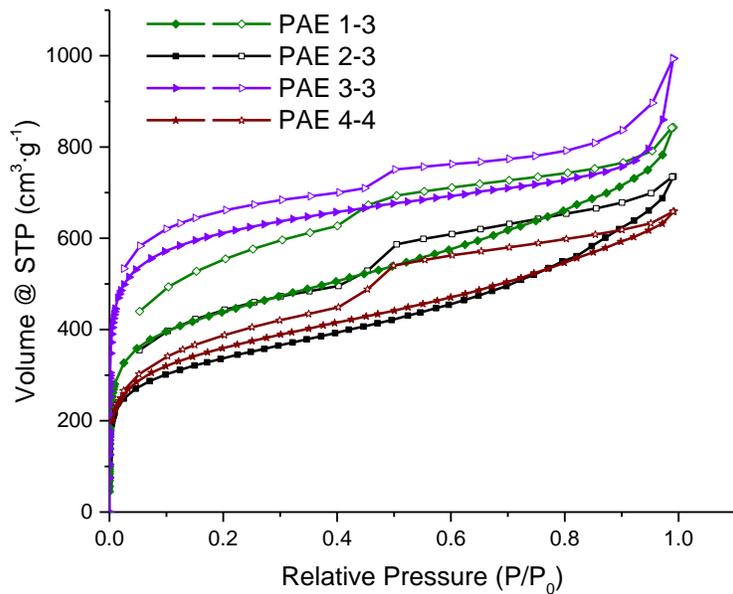


Figure S11. N₂ adsorption (filled symbol) and desorption (open symbol) isotherms for PAE series containing tetrahedral-shaped monomers.

7. Pore size distribution of PAE series

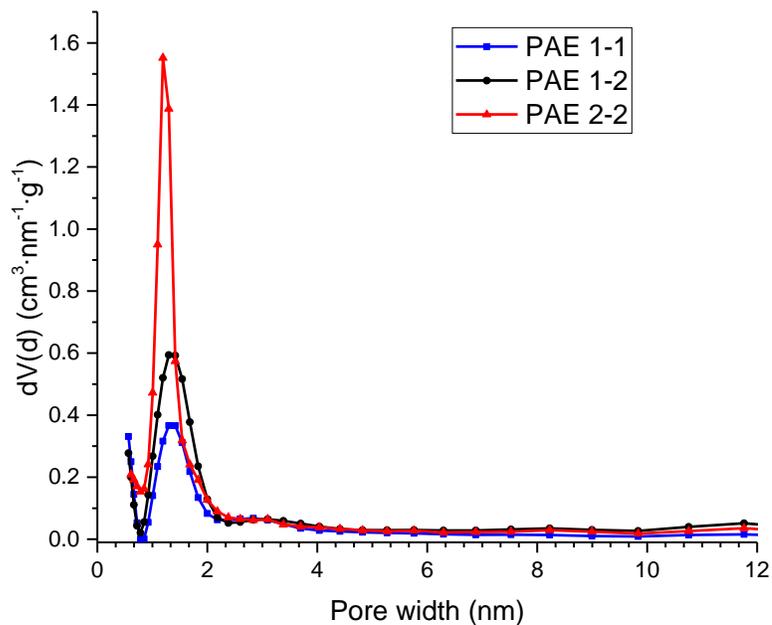


Figure S12. Pore size distribution profiles of PAE series containing planar monomers **1** and **2**.

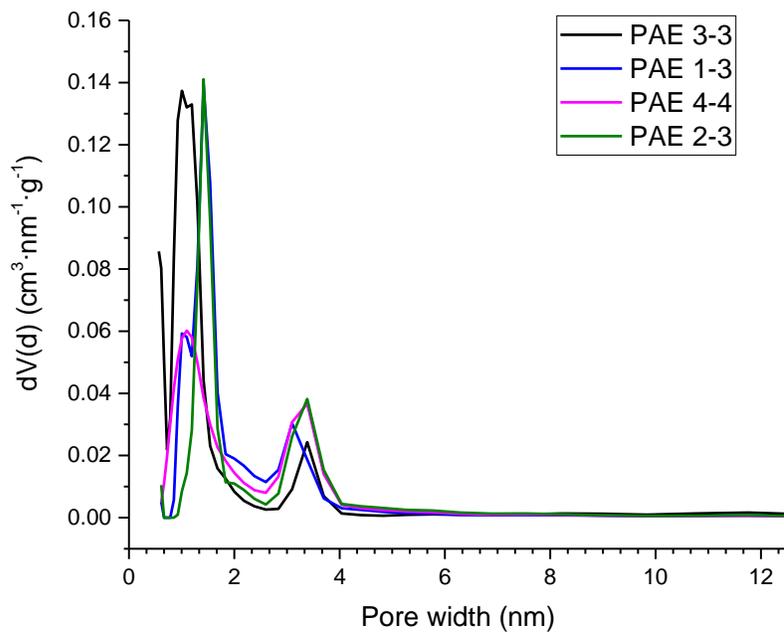


Figure S13. Pore size distribution profiles of PAE series containing tetrahedral-shaped monomers.

8. Solid State NMR of the as synthesized networks

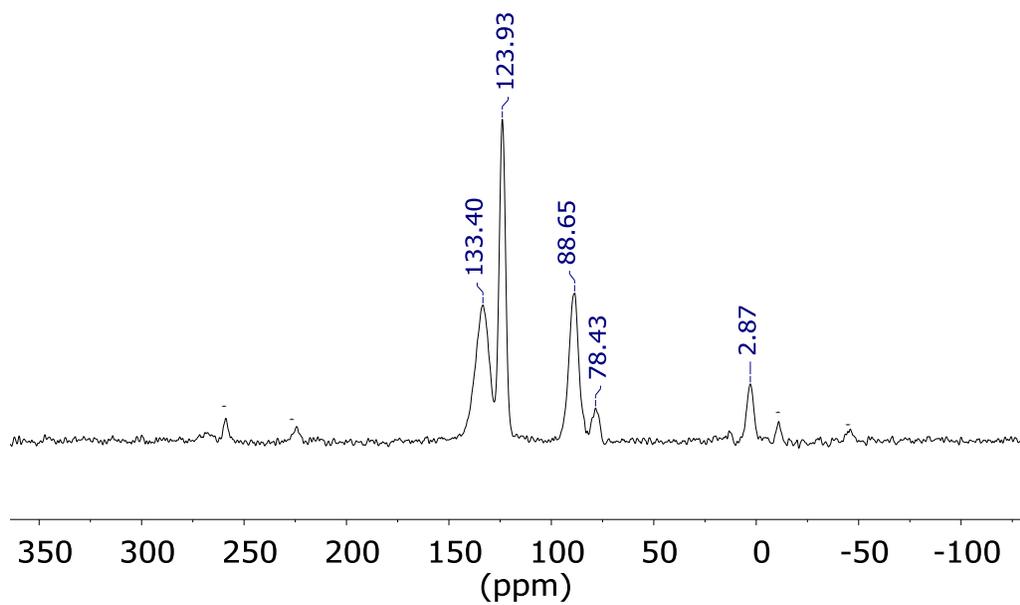


Figure S14. ^{13}C -CPMAS of the PAE 1-1

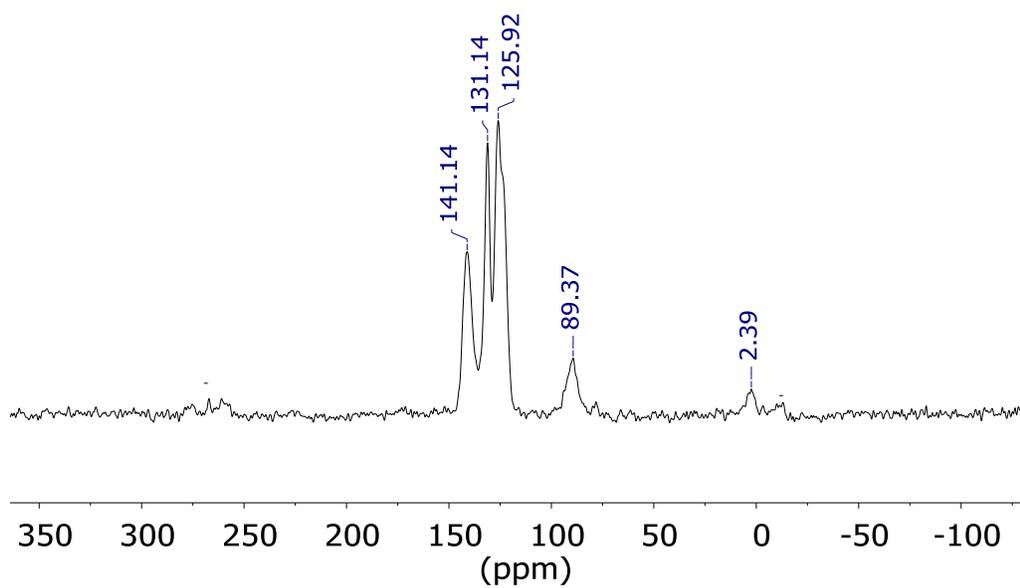


Figure S15. ^{13}C -CPMAS of the PAE 1-2.

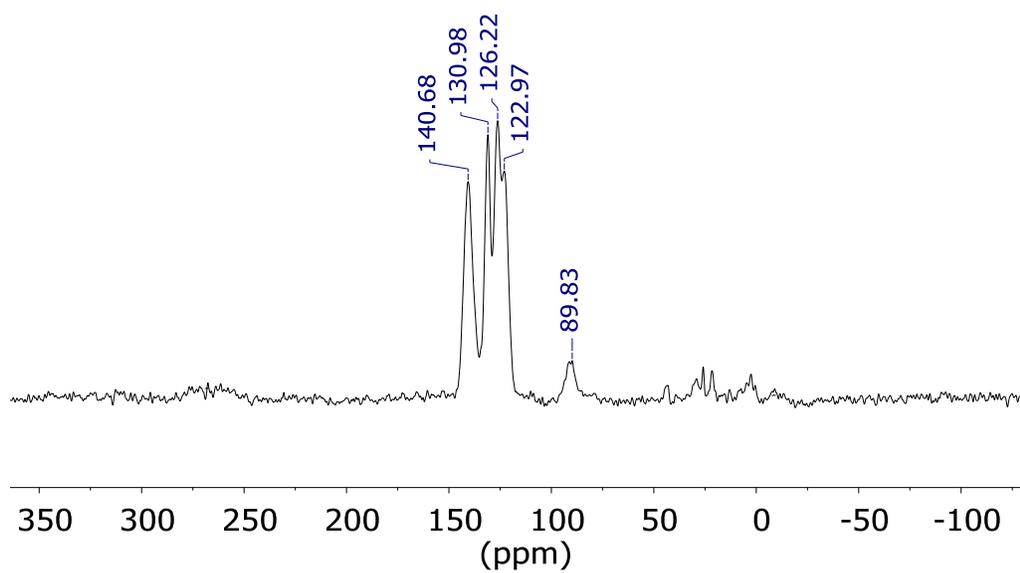


Figure S16. ^{13}C -CPMAS of the PAE 2-2.

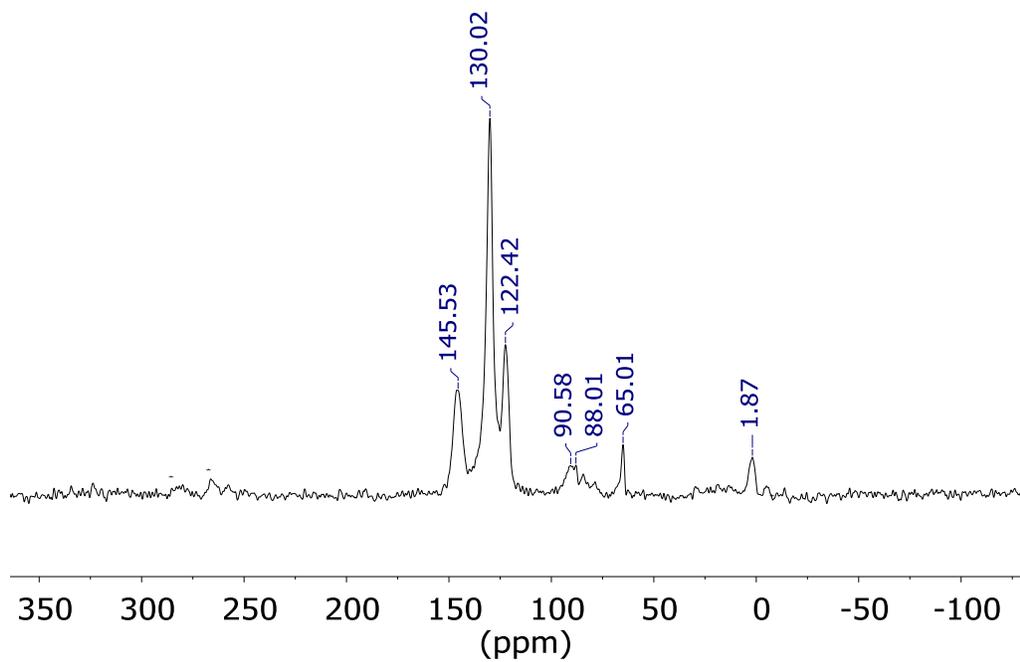


Figure S17. ^{13}C -CPMAS of the PAE 3-3.

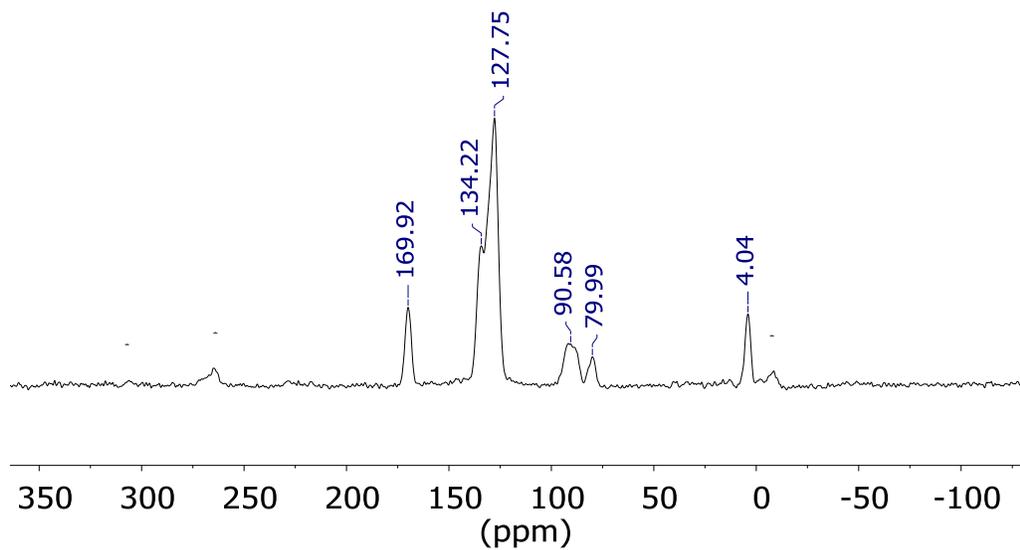


Figure S18. ^{13}C -CPMAS of the PAE 4-4.

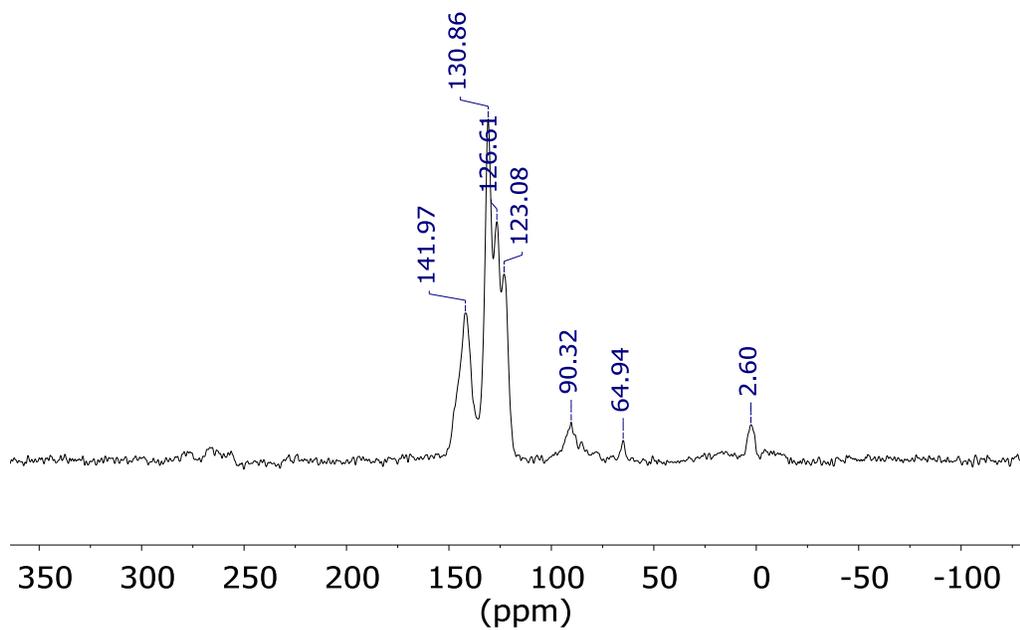


Figure S19. ^{13}C -CPMAS of the PAE 1-3.

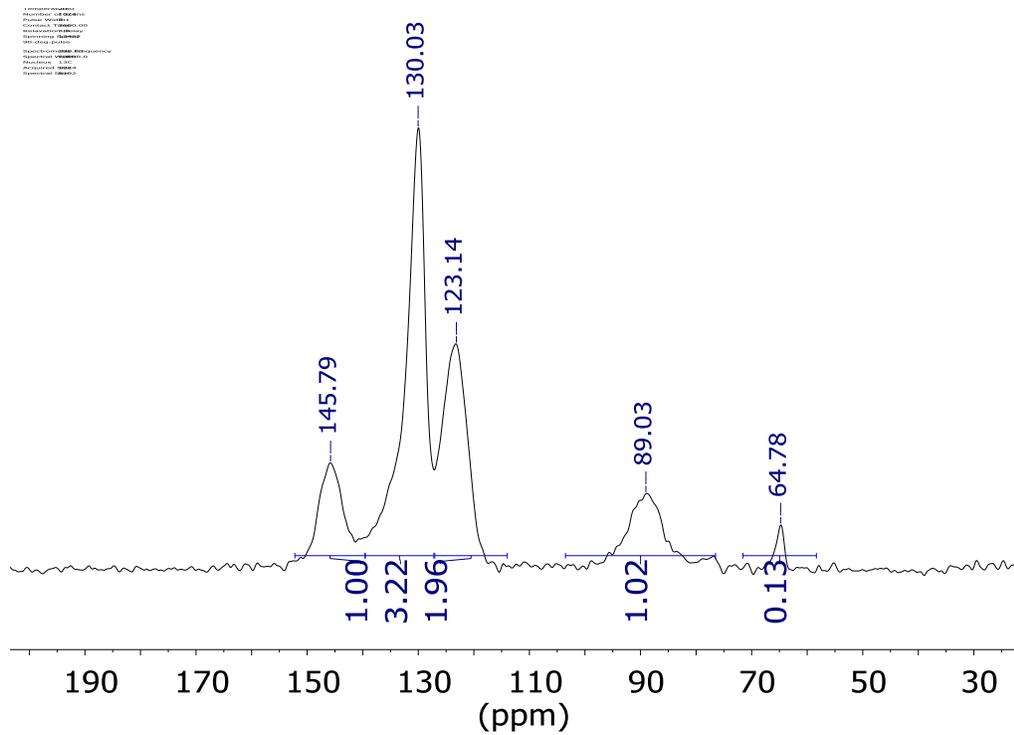


Figure S20. ^{13}C -CPMAS of the PAE 2-3

9. SEM images of PAE series

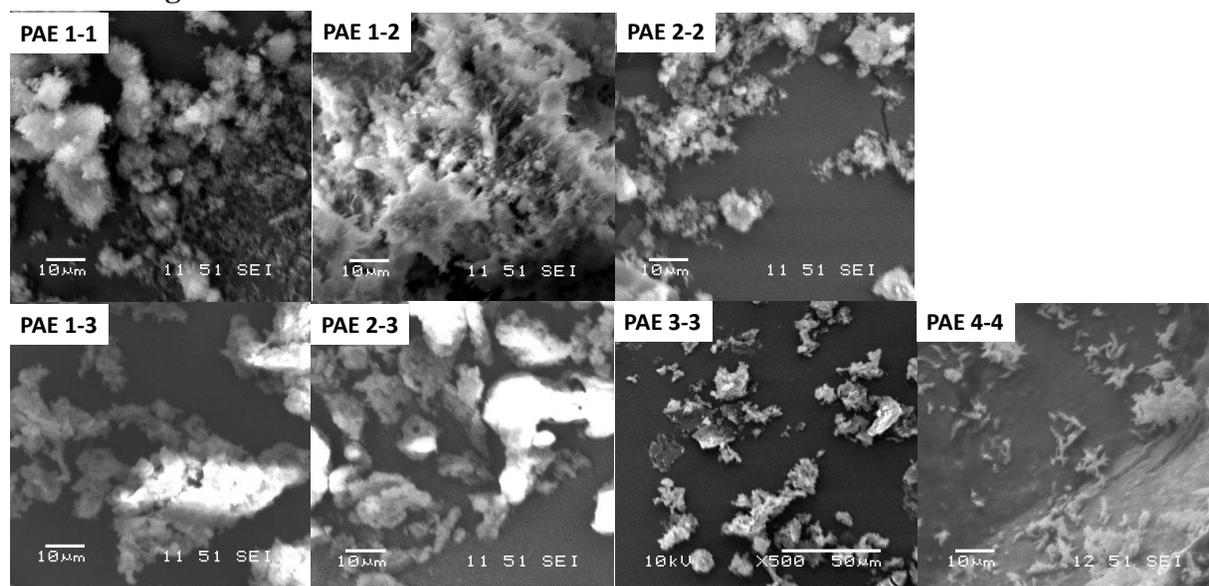
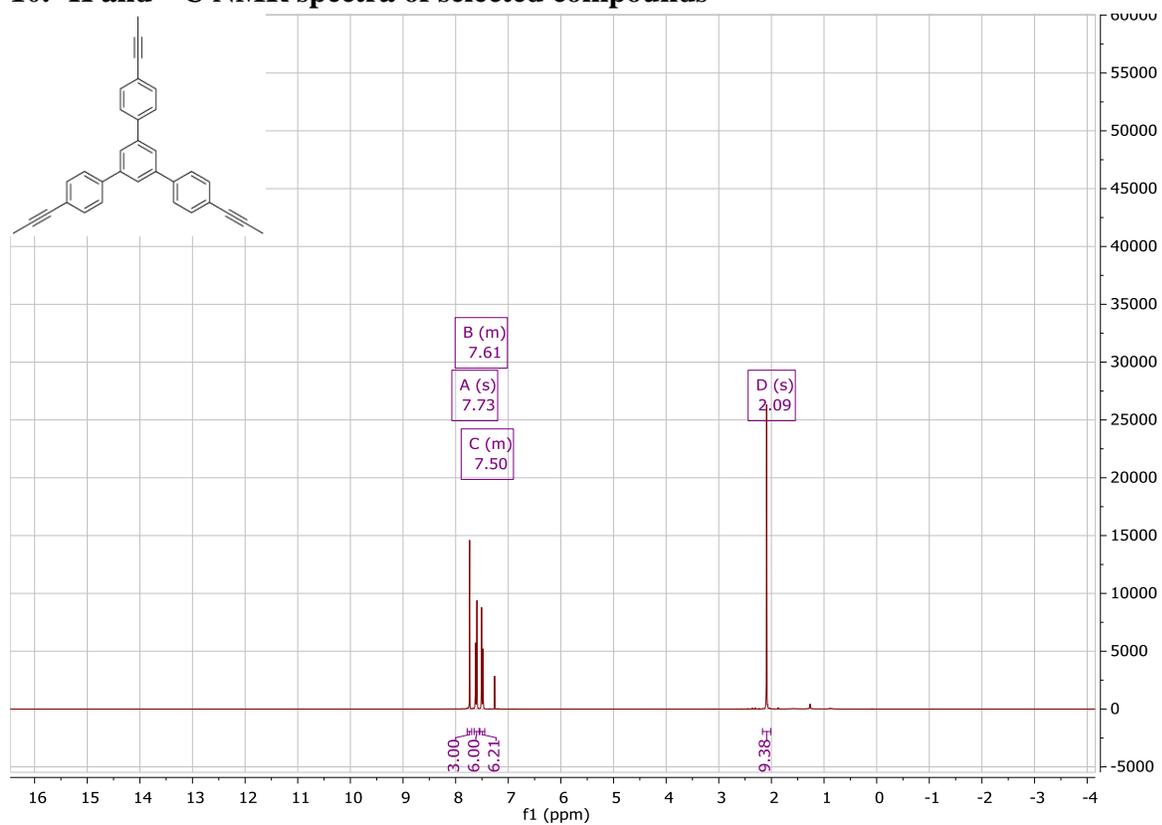
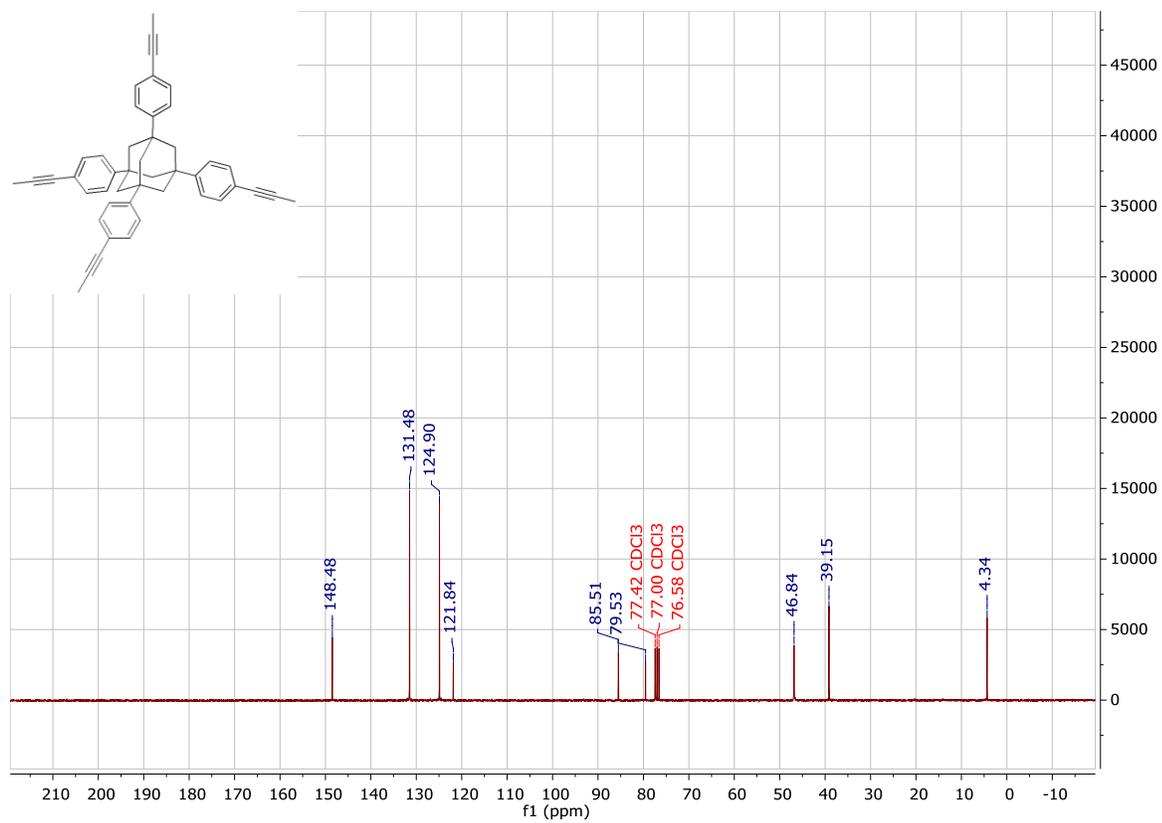


Figure S21. SEM images of PAEs

10. ¹H and ¹³C NMR spectra of selected compounds





11. References

- (1) Liu, J.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Organometallics* **2009**, *28*, 413.
- (2) Zhu, Y.; Yang, H.; Jin, Y.; Zhang, W. *Chem. Mater.* **2013**, *25*, 3718.