

Supporting Information

Extended phenylene based microporous organic polymers with selective carbon dioxide adsorption

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1. Synthesis:

Compounds **3** and **4** were synthesized according to the literature methods¹ and benzene 1,4-diboronic acid (BDDBA) was purchased from Aldrich.

Exact procedure for synthesis of *p*-PPF and *m*-PPF. A mixture of tribromo derivative (0.46 mmol) and 1,4-benzene diboronic acid (0.92 mmol) in DMF (20 mL) was degassed by four freeze-pump-thaw cycles. To this mixture 2M K₂CO₃ in water (4 mL) and tetrakis(triphenylphosphine)-palladium(0) (70 mg, 60.6 μmol) were added followed by degassing by four freeze-pump-thaw cycles. After that the resultant mixture was purged with Ar and stirred at 150 °C in a schlenk flask for 36 h. After cooling to room temperature the mixture was poured into water and filtered. The precipitate was washed with methanol, dichloromethane and dried in vacuum. The precipitate was further purified by soxhlet extractions with water, methanol, dichloromethane and tetrahydrofuran for 12 h each.

***p*-PPF**: Grey solid (250 mg). Solid-state ^{13}C NMR (δ ; ppm): 138.8, 130.3, 126.2 ppm. FT-IR (ν ; cm^{-1}): 3408, 3055, 3023, 1590, 1481, 1381, 1117, 1010, 869, 837, 786, 699. Elemental Analysis (%) Calcd. For $\text{C}_{42}\text{H}_{26}$: C 95.09, H 4.91; Found: C, 85.62; H, 4.14.

***m*-PPF**: Grey solid (260 mg). Solid-state ^{13}C NMR (δ ; ppm): 145.4, 131.6 ppm. FT-IR (ν ; cm^{-1}): 3417, 3053, 3027, 1592, 1472, 1379, 1121, 1010, 875, 835, 782, 701. Elemental Analysis (%) Calcd. For $\text{C}_{42}\text{H}_{26}$: C 95.09, H 4.91; Found: C, 85.72; H, 4.24.

References.

- (1) S. Kotha, D. Kashinath, K. Lahiri, R. B. Sunoj, *Eur. J. Org. Chem.* 2004, 4003.

2. Supporting Figures.

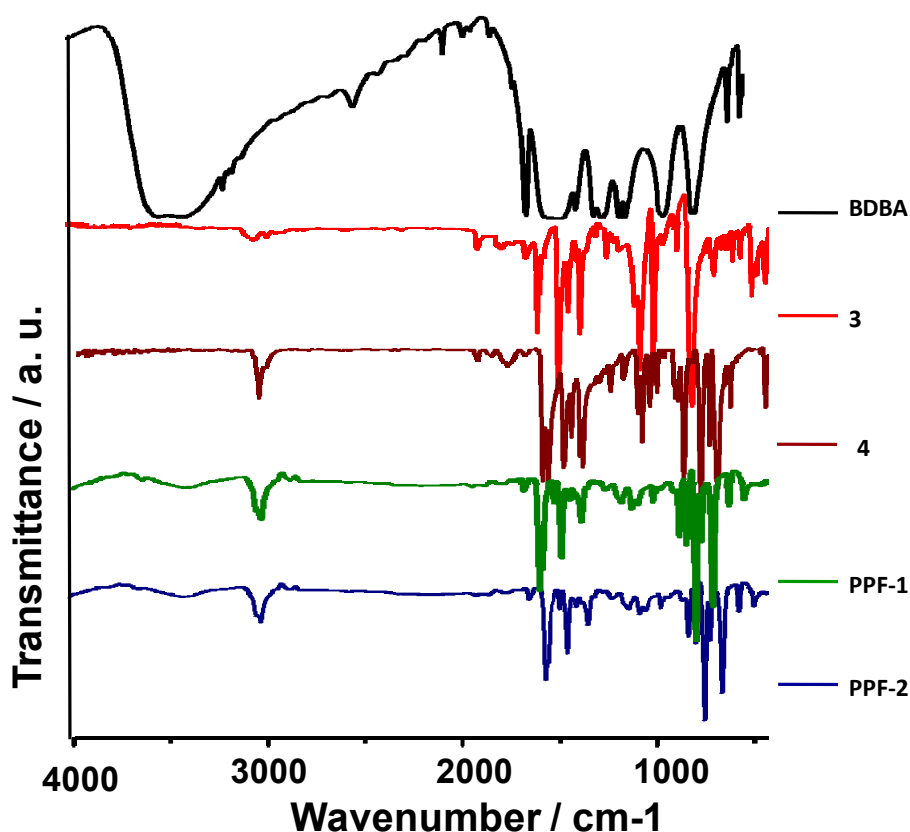


Fig. S1 FT-IR spectrum of BDBA, 3, 4, *p*-PPF and *m*-PPF.

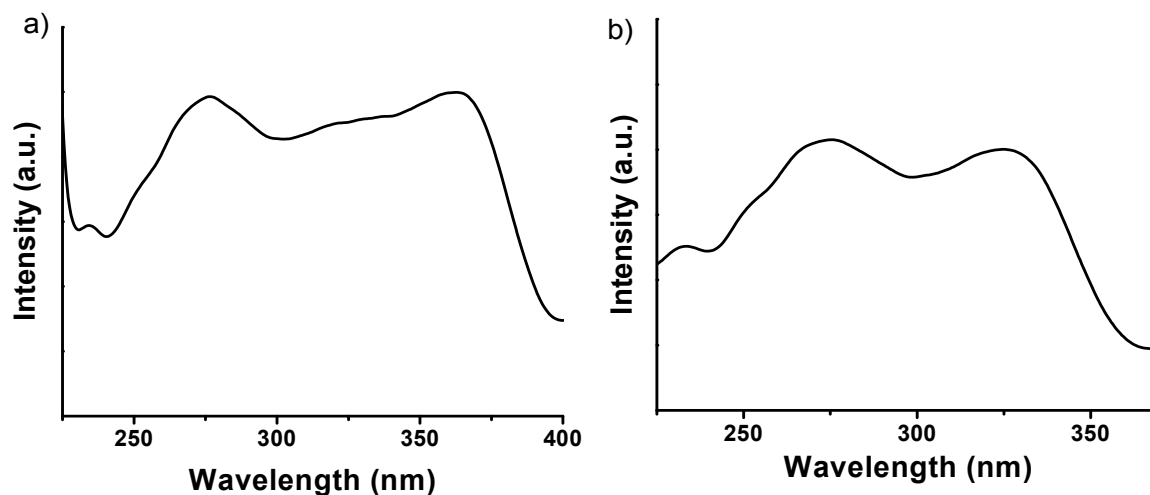


Fig. S2 Excitation spectra of a) *p*-PPF ($\lambda_{\text{em}} = 430$ nm) and b) *m*-PPF ($\lambda_{\text{em}} = 400$ nm).

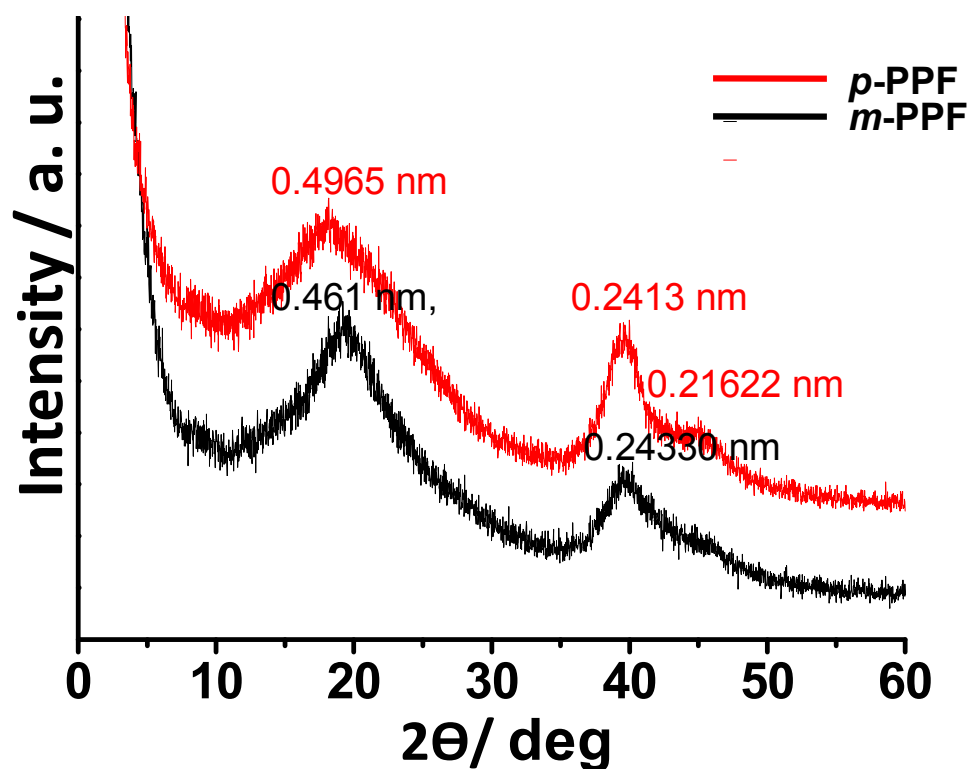


Fig. S3 Powder XRD analyses of *p*-PPF and *m*-PPF with d-values.

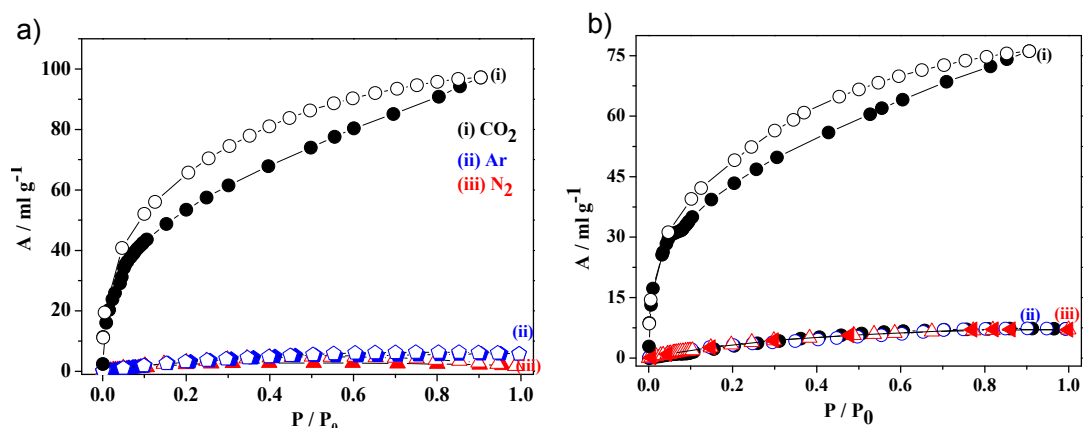


Fig. S4 Sorption isotherms for: (a) *p*-PPF and (b) *m*-PPF at 195 K (empty symbols shows adsorption, filled symbols shows desorption, P_0 is the saturated vapor pressure of the respective adsorbates). The measurements are done with a 360 seconds equilibrium time.

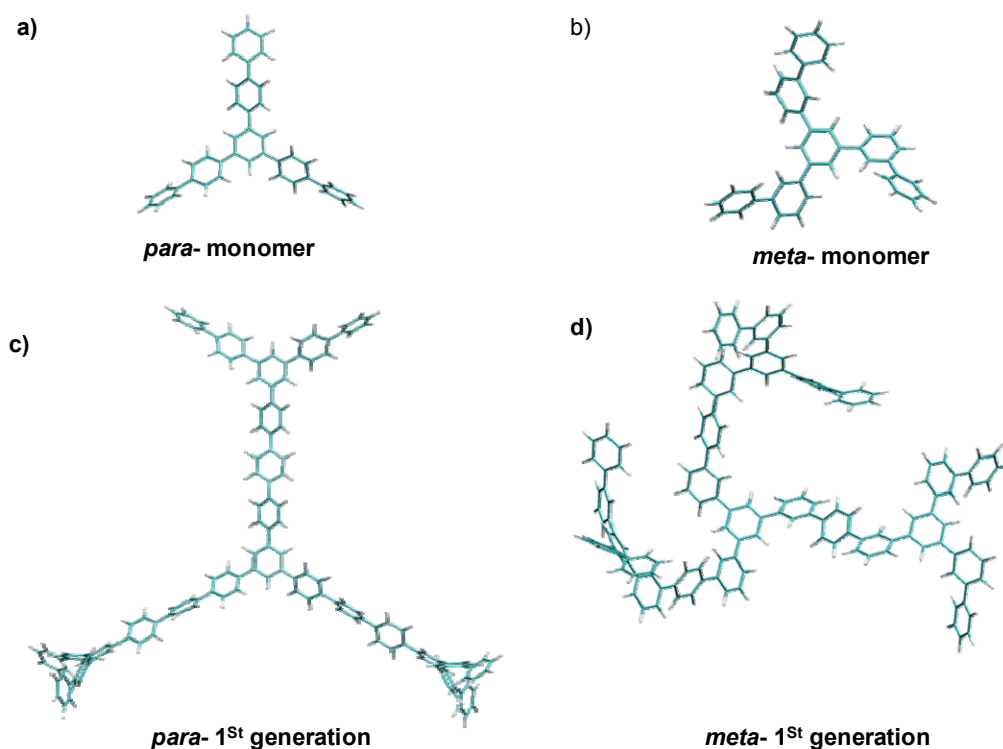


Fig. S5 Energy minimized structures of (a), (b) the monomers and (c), (d) the first generation of the polymers (*p*-PPF and *m*-PPF) calculated from Gaussian-09 suite of programs.¹

References.

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford, CT, 2010.