Supporting Information

Enhanced hydrogen storage and carbon dioxide uptake and selectivity of indole-based microporous organic polymer

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Table of contents

I.	Simulation Method.	S3
II.	Synthesis and characterization of 1,3,5-tris-(4-fluorobenzoyl)benzene	S4-6
III.	XPS data	S7
IV.	Thermal stability of microporous PINK	S7
V.	Three-dimensional structures of microporous PINK	S8
VI.	BET specific surface area plots of PINK	S9
VII	Gas adsorption isotherms of PINK	S10
VII	I. Isosteric heat of CO2 adsorption for PINK	S11

I. Simulation Method

In this study, molecular models were performed on the Amorphous Cell module of the Materials Studio program (MS, version 4.4, Accelrys Software Inc., USA). The "Dreiding force field" was used. A single parent chain with 18 repeat units was generated originally. Although the system size of 18 repeat units is not enough to represent conformations of a real branched polymers, previous researchers have reported reasonable results when they used 10-15 repeat units for rigid polymer simulation.^[1] Then, periodic boundary conditions were imposed and an initial density of 0.6 g/cm³ was used to simulate the bulk aggregation structure for model PINK polymer. Each initial structure was optimized by a molecular mechanics (MM) technique using the conjugate gradient method. Because this optimized structure might, however, be still in a local energy minimum state, it was relaxed through NVT molecular dynamics (MD) (In the canonical ensemble, mole (M), volume (V), and temperature (T) are conserved), the time evolution of chain conformations up to 1000 ps with time steps of 0.0002 ps at 800 K. This hightemperature relaxation procedure was suggested by Lee et al.^[2] To obtain a suitable structure for further MD simulation, we built and relaxed 10 different initial structures for each system according to the procedure mentioned previously. Only one structure with the lowest energy for each system was selected as the sample structure for the further research.

II. Synthesis and characterization of 1,3,5-tris-(4-fluorobenzoyl) benzene

To a one-necked flask equipped with magnetic stirrer, 1,3,5-benzenetricarbonyl trichloride (0.05 mol), fluorobenzene (0.95 mol), anhydrous AlCl₃ (0.12 mol) were added. The reaction mixture was stirred 12 h at room temperature, and then heated to 90 °C under stirring for 2h. The resulting solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water 5 times. The crude material was recrystallized from *N*,*N*-dimethylacetamide (DMAc) to afford 1,3,5-tris-(4-fluorobenzoyl)benzene as colorless crystals. Yield: 98%; M.p. 207 °C; FT-IR spectrum (KBr pellet, cm-1): 1664, 1597, 1500, 1406, 1253, 1157, 1008, 849, 751, 599; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.22 (s, 3H), 7.94 (s, 6H), 7.43 (t, J = 8.0 Hz, 8.0 Hz, 6H) ppm; ¹³C NMR (150 MHz, DMSO-d6): δ = 116.0, 132.9, 133.7, 1137.4, 163.8, 166.3, 192.9 ppm; HRMS (ESI): calcd for C₂₇H₁₅F₃O₃ [M+H]+: 445.0973, found: 445.0947; Anal. Calcd for C₂₇H₁₅F₃O₃: C, 72.97; H, 3.38; Found: C, 72.91; H, 3.39.



Scheme S1. Synthesis of 1,3,5-tris-(4-fluorobenzoyl) benzene.



Fig. S1. FT-IR of 1,3,5-tris-(4-fluorobenzoyl) benzene.



Fig. S2. ¹H NMR of 1,3,5-tris-(4-fluorobenzoyl) benzene.



Fig. S3. ¹³C NMR of 1,3,5-tris-(4-fluorobenzoyl) benzene.

III. XPS data



Fig. S4. XPS data of PINK (C and F atoms).

IV. Thermal stability of microporous PINK



Fig. S5. TG curve of PINK in nitrogen.

V. Three-dimensional structures of microporous PINK



Fig. S6-1. The Three-dimensional pore structures of PINK.



Fig. S6-2. The Three-dimensional network of hypercrosslinked PINK.

VI. BET specific surface area plots of PINK



Fig. S7. BET specific surface area plots of PINK



VII. Gas adsorption isotherms of PINK

Fig. S8. Gas adsorption isotherms of PINK: (a), 291 K; (b), 308 K.

VIII. Isosteric heat of CO2 adsorption for PINK



Fig. S9. CO2 adsorption isotherms of PINK at different temperatures (a); Isosteric heat of CO2 adsorption for PINK (b)

References

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