

Electronic Supplementary Information

A Succinct Strategy for Construction of Nanoporous Ionic Organic Networks from a Pirylium Intermediate

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Experimental Procedures

1. Materials

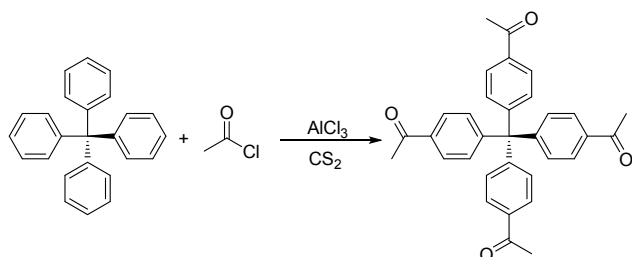
All reagents and solvents were purchased from commercial sources (Fisher scientific and Sigma-Aldrich) and were used without further purification, unless indicated otherwise. Tetrakis(4-acetylphenyl)methane (A) and 9,9'-Spirobi[9H-fluorene]-2,2',7,7'-tetracarboxaldehyde (B) were synthesized according to the previously reported procedures.

2. Characterization

Liquid ^1H and ^{13}C NMR spectra was recorded on Bruker 400 MHz NMR spectrometer. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1} . ^{13}C solid-state NMR was performed using a Solid State Varian INOVA 400 MHz. X-ray photoelectron spectroscopy (XPS) measurements: XPS experiments were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV. Samples were mounted on In foil since the C1s binding energy was used to calibrate the binding energy shifts of the sample (C1s = 284.8 eV). The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini 2360 surface area analyzer. The samples were outgassed at 150 °C for 16 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. TGA curves were collected by a TA Q50 thermogravimetric analyzer under air (100 ml/min) with a ramping rate of 10 °C/min.

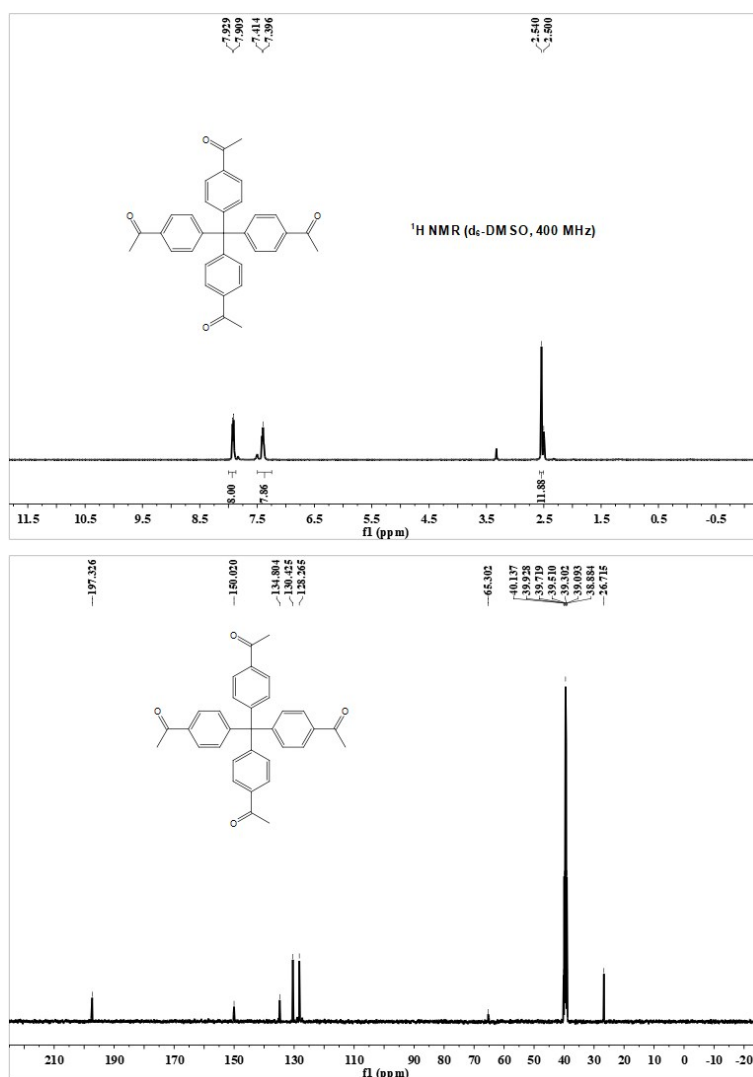
3. Synthesis of Monomers

Synthesis of tetrakis(4-acetylphenyl)methane

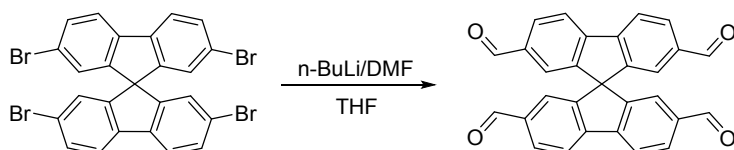


To a mixture of tetraphenylmethane (0.32 g, 1 mmol), acetyl chloride (0.40 g, 5.1 mmol) and carbon disulfide (50 mL), aluminium chloride (0.67 g, 5.03 mmol) was added, and the mixture was heated to 60 °C for 18 h. After cooling, carbon disulfide was decanted and ice, concentrated hydrochloric acid and dichloromethane were added subsequently to the precipitate. The mixture was stirred until the precipitate completely dissolved. Then the organic layer was dried with sodium sulfate and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel (dichloromethane/n-hexane) to give tetrakis(4-acetylphenyl)methane (0.40 g) as a colorless powder (yield: 83%).

^1H NMR (d_6 -DMSO, 400 MHz) δ 2.54 (s, 12H), 7.40 (d, $^3J = 7.2\text{ Hz}$, 8H), 7.92 (d, $^3J = 8\text{ Hz}$, 8H); ^{13}C NMR (d_6 -DMSO, 100.6 MHz) δ 26.72, 65.30, 128.26, 130.42, 134.80, 150.02, 197.33.



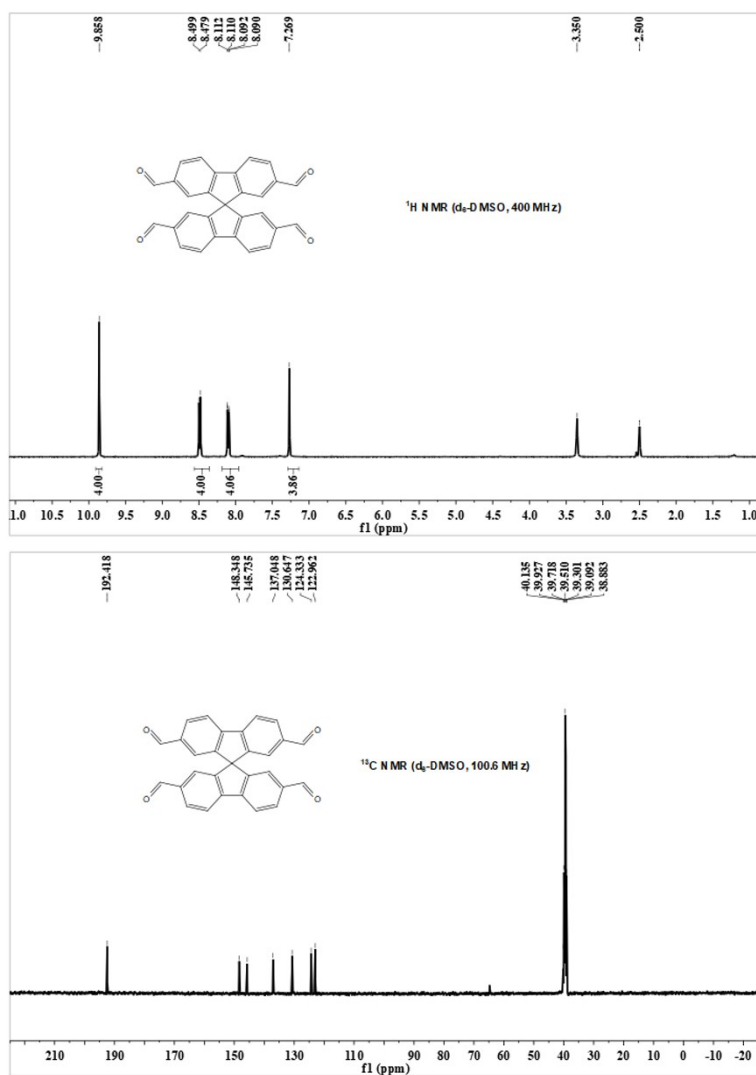
Synthesis of 9,9'-spirobi[fluorene]-2,2',7,7'-tetracarbaldehyde



A solution of 2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] (2.2 g, 3.5 mmol) in anhydrous THF (300 mL) was cooled with a dry ice/acetone bath ($-78\text{ }^{\circ}\text{C}$) under dry argon. To the resulting suspension, a solution of n-BuLi (13.0 mL, 2.5 M in hexanes, 32.5 mmol) was added dropwise over a period of 10 minutes. The resulting clear yellow solution was stirred at $-78\text{ }^{\circ}\text{C}$ for an additional 1 hour. Anhydrous DMF (5.0 mL, 64 mmol) was added dropwise over 10 minutes, and the cooling bath was removed. The reaction mixture allowed to warm up to room temperature and was stirred overnight. The resulting solution was treated with 1 M aqueous HCl (40 mL), and volume of the liquid was decreased to ca 1/3 using rotary evaporator under vacuum. The obtained 2 phase mixture was treated with ethyl acetate (100 mL) and hexanes (100 mL), resulting in precipitation of white solid. Solid material was separated by filtration and was air dried before being dry-absorbed on silica gel. After purification using column chromatography on silica gel (gradient hexanes/ethyl acetate, 0 % to 100 % of ethyl acetate) and evaporation of solvent from the fractions containing the product, the title compound was obtained as a white solid (400 mg, 27 % yield).

^1H NMR (d_6 -DMSO, 400 MHz) δ 7.27 (s, 4H), 8.09~8.11 (m, 4H), 8.48 (d, $^3J = 8$ Hz, 4H), 9.86 (s, 4H); ^{13}C NMR (d_6 -DMSO, 100.6 MHz)

122.96, 124.33, 130.65, 137.05, 145.74, 148.35, 192.42.



4. Preparation of polymers

(1) Synthesis of Py-POP

Tetrakis(4-acetylphenyl)methane (0.1953 g, 0.4 mmol), 9,9'-spirobifluorene-2,2',7,7'-tetracarbaldehyde (0.0857 g, 0.2 mmol) was added to a schlenk tube with volume of 25 mL. Then 1,4-dioxane (8 mL) was added and the monomers were dissolved under stirring at room temperature. BF₃·Et₂O (0.35 mL) solution was added to the mixture. The schlenk tube was sealed and freeze-pump-thaw was conducted and repeated for three times. The mixture was slowly warmed up to room temperature and then to 120 °C in an oil bath for 72 h. After reaction, the mixture was treated through filtration and the collected solid was thoroughly washed with distilled water, tetrahydrofuran (THF) and ethanol, the desired polymer was collected and dried in vacuum oven at 100 °C for 24 h, and obtained as yellow solids. The yield calculated based on the added monomers was 65%.

(2) Synthesis of HE-Py-NION

The following items are added to a schlenk tube with volume of 25 mL successively: the previously prepared pyrylium-functionalized polymer (Py-POP) (0.06 g), anhydrous EtOH (10 mL) and ethanolamine (0.24 g, 4 mmol). Then the schlenk tube is

sealed and freeze-pump-thaw is conducted for one cycle. The reaction mixture is warmed up to room temperature and then heated to 100 °C in an oil bath for 24 h. After the reaction, the mixture is cooling down to room temperature and treated with filtration, the solid is washed thoroughly with tetrahydrofuran and ethanol. The resultant materials are obtained as yellow solids after drying at 100 °C under vacuum for 24 h. Almost quantitative yields are obtained based on the weight of the starting polymers.

5. The dye adsorption experiment

Methylene blue hydrate (MB) dye was formulated into an alcohol solution with a concentration of 0.025 mM. 3 mg polymer Py-POP and HE-Py-NION were added separately into the 3mL MB solution and corresponding UV spectra of supernatant solution were recorded by the change of time. The following equation was used to calculate the absorption rate of MB,

$$R_t = A_t / A_0 * 100\%$$

Where R_t is absorption residual capacity, A_0 is the initial absorbance of the solution and A_t is the absorbance at the specific time.

6. Time dependent study of oxo-anion KMnO_4 removal

In the case of the MnO_4^- removal study, 5 mM MnO_4^- solution (2 mL) was taken into a cuvette and the initial absorption was recorded by UV-vis spectroscopy. Then, 2.6 mg polymer HE-Py-NION was added into the cuvette and stirred. The corresponding UV spectra of supernatant solution was recorded at different time intervals. The % removal and decrease in the concentration of MnO_4^- vs. time was calculated using the following equation.

$$D_t = (A_0 - A_t) / A_0 * 100\%$$

Where D_t is exchange capacity, A_0 is the initial absorbance of the solution and A_t is the absorbance at the specific time.

7. Calculation of KMnO_4 adsorption capacity

5 mg of polymer HE-Py-NION was added into 10 mL 5 mM KMnO_4 solutions for 24h with stirring. Then, supernatant solution was used for further UV-Vis measurement after centrifuge. The KMnO_4 capacity of polymer was calculated by initial and final UV absorbance. Computation formula was as follows,

$$C = (C_0 - C_t) * V * M_{\text{KMnO}_4} / m$$

Where C is the KMnO_4 capacity, C_0 is the initial KMnO_4 concentration of the solution, C_t is the final KMnO_4 concentration of the solution, V is the volume of solution, M_{KMnO_4} is molecular weight of KMnO_4 and m is the mass of polymer HE-Py-NION.

The experiment was repeated three times and the result (1.145 g KMnO_4 /g HE-Py-NION) is the average of the repeated experiment.

9. Supplementary figures

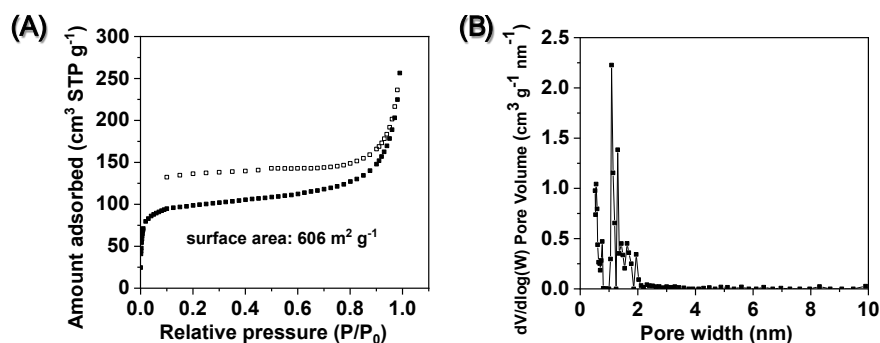
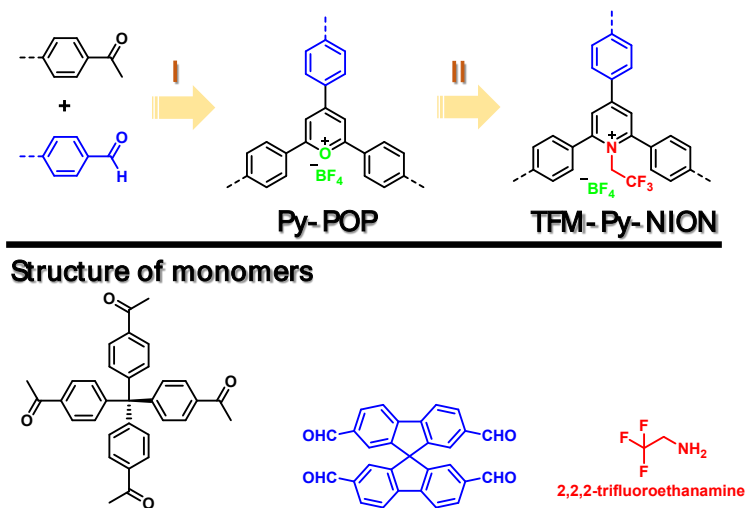


Figure S1. (A) N_2 sorption/desorption isotherm analysis of Py-POP at 77 K. (B) Pore size distribution in Py-POP.



Scheme S1. Synthetic pathway of TFM-Py-NION, and structure of the monomers.

Reaction conditions: step I $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 1,4-dioxane, 120°C , 72 h; step II 2,2,2-trifluoroethanamine, ethanol, 100°C , 24 h. The synthetic procedure was similar to that of HE-Py-NION, but with different amine in the second step.

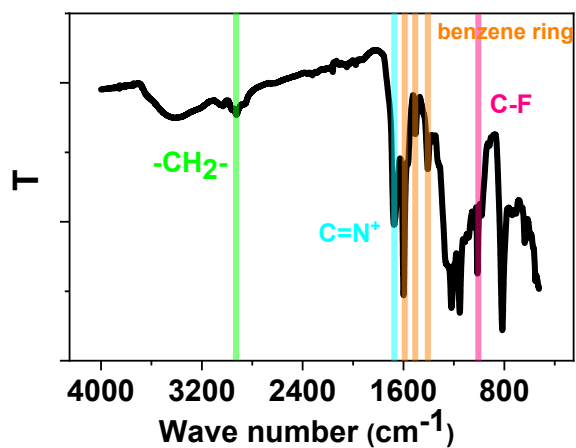
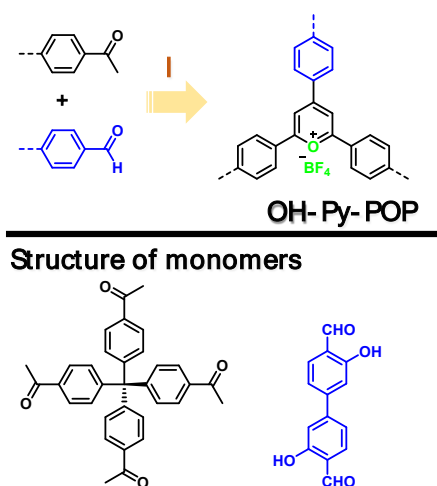


Figure S2. FTIR spectra of TFM-Py-NION.



Scheme S2. Synthetic pathway of OH-Py-POP and structure of the monomers.

Reaction conditions: step I $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 1,4-dioxane, 120 °C, 72 h. The synthetic procedure was similar to that of Py-POP, but with different aldehyde.

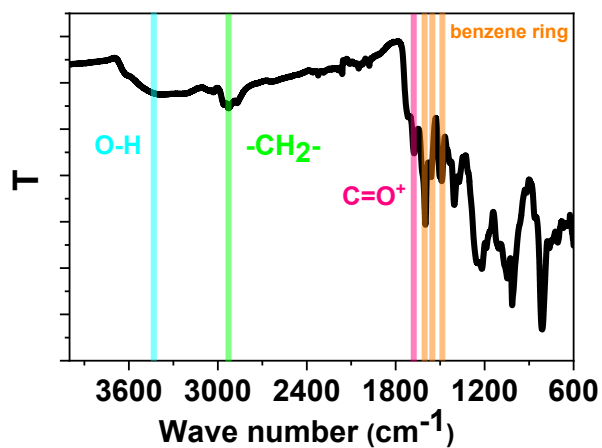


Figure S3. FTIR spectra of OH-Py-POP.

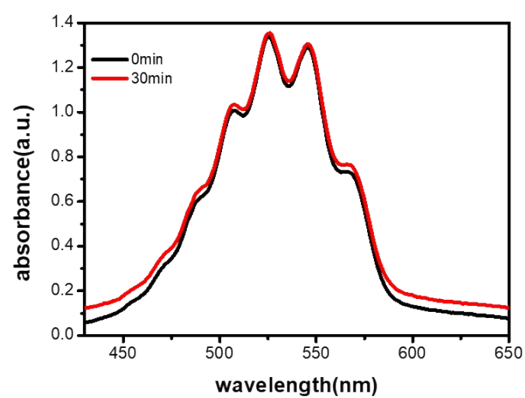


Figure S4. UV-Vis spectroscopy in the presence of Py-POP (1 mg) for the water solution of MnO₄⁻ (0.5 Mm, 2 mL).