Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information (ESI) for

All-thiophene-based conjugated porous organic polymers

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Synthesis of 2,2′-dibromo-3,3′-bithiophene.

To the solution of 3,3′-dithiophene (3.33 g, 19.8 mmol) in dichloromethane (30.0 mL), acetic acid (20.0 mL) and *N*-bromosuccinimide (6.02 g, 33.8 mmol) were added. The reaction was monitored by TLC analysis. After 3,3′-bithiophene was completely consumed, the reaction mixture was quenched with water, extracted with saturated aqueous sodium bicarbonate solution, and water, respectively, and then dried over anhydrous magnesium sulfate. The crude product was purified by silica chromatography with petroleum ether as an eluent to generate white solid (5.9 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, *J*=5.2 Hz, 2H), 7.09 (d, *J*=5.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ135.3, 129.1, 125.6, 111.1.

Synthesis of cycloocta[1,2-*b*:4,3-*b*′:5,6-*b*′′:8,7-*b*′′′]tetrathiophene (COTh).

tert-Butyllithium (1.10 mL, 2.48 M, 2.71 mmol) was added to a solution of 2,2′-dibromo-3,3′-bithiophene (0.39 g, 1.23 mmol) in anhydrous ethyl ether (80.0 mL), cupric chloride (0.41 g, 3.1 mmol) was added after the reaction mixture was kept at –78 °C for 2 h. The reaction mixture was kept at –78 °C for 2 h, and then slowly warmed to and kept at room temperature overnight. The reaction mixture was quenched with methanol, extracted with ether, washed with water, and then finally dried over anhydrous magnesium sulfate. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether as eluent. A white solid was obtained (0.13 g, 20%). Mp: 254–255 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (d, *J*=5.2 Hz, 4H), 6.96 (d, *J*=5.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ136.6, 132.4, 129.9, 127.1. EI-MS *m/z* = 328 (M^+).

Synthesis of 1,3,5-trichloro-2,4,6-triiodobenzene.

Periodic acid (6.945 g, 30.7 mmol) and iodine (23.2 g, 91.4 mmol) were dissolved with concentrated sulfuric acid (200 mL). 1,3,5-trichlorobenzene (3.32 g, 18.3 mmol) was added slowly after stirring for 15 min. the reaction was stirred for 30 h. the mixture was poured into ice-water. The residue was collected by vacuum filtration and washed with solution aqueous sodium sulfite solution in order to remove iodine, then washed with water, methanol, and ether. A white solid product (9.5061 g, 93% yield) can be got.

Synthesis of 1,3,5-trichloro-2,4,6-tris[(trimethylsilyl)ethynyl]benzene.

Under nitrogen, 1,3,5-trichloro-2,4,6-triiodobenzene (4.02 g, 7.20 mmol), cuprous iodide (0.12 g, 0.65 mmol) and bis(triphenylphosphine)palladium (II) dichloride (0.45 g, 0.65 mmol) were dissolved in a mixture of anhydrous diisopropylamine/tetrahydrofuran (30.0 mL/30.0 mL), then trimethylsilylacetylene (3.8 mL, 25.91 mmol) was added via a syringe. The reaction mixture was stirred for 20 h at 40 °C. After cooling to room temperature, solvent was removed in vacuum, and dichloromethane was added to dissolve the residue and aqueous phase was extracted with dichloromethane, then dried over anhydrous magnesium sulfate. The crude product was purified by silica chromatography with petroleum ether as an eluent. A yellow solid (1.31 g, 40 %) was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): d0.29 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ139.1, 122.7, 108.1, 97.4.

Synthesis of benzo[1,2-*b*:3,4-*b′*:5,6-*b′′*]trithiophene (BTTh).

Sodium sulfide nonahydrate (1.88 g, 7.85 mmol) was crushed and added to 1-methyl-2-pyrrolidinone (30.0 mL), and then 1,3,5-trichloro-2,4,6-tris[(trimethylsilyl)ethynyl]benzene (0.62 g, 1.31 mmol) was added to the suspension. The reaction mixture was stirred for 10 h at 150 °C. After cooling to room temperature, the reaction mixture was poured into saturated aqueous ammonium chloride (150.0 mL). The residue was collected by filtration and diluted by dichloromethane. The solution was washed with brine and dried over anhydrous magnesium sulfate. The crude product was purified by silica chromatography with petroleum ether as an eluent. A white solid (0.17 g, 51.8%) was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.64 (d, *J*=5.2 Hz, 3H), 7.54 (d, *J*=5.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ131.9, 131.6, 125.1, 122.4. EI-MS *m/z* = 246 (M^+).

Table S1. Oxidation polymerization using **BTTh** and different equivalent ferric chloride.

Run	**COTh** (mg)	$FeCl_3$ (mg)	Molar ratio [a]	**ThPOP-1** (mg)	Yield (%)	Cl (at%)	S_{BET} ($m^2\ g^{-1}$)
1	55	543.0	5.0	61.6	112	6.997	838
2	55	217.2	2.0	54.2	98.5	4.602	917
3	55	130.3	1.2	53.9	98.0	1.334	1050

[a] Molar ratio of ferric chloride and single reaction site of **COTh**.

Table S2. Oxidation polymerization using **BTTh** and different equivalent ferric chloride.

Run	**BTTh** (mg)	$FeCl_3$ (mg)	Molar ratio [b]	**ThPOP-2** (mg)	Yield (%)	Cl (at%)	S_{BET} ($m^2\ g^{-1}$)
1	55	543.0	5.0	59.4	108	7.863	123
2	55	217.2	2.0	53.2	96.7	5.893	127
3	55	130.3	1.2	54.4	97.0	2.391	160

[b] Molar ratio of ferric chloride and single reaction site of **BTTh**.

Table S3. Summary of the hydrogen uptake capacities at low pressure and sulfur content of microporous organic polymers.

Porous materials	S_{BET} (m^2 g^{-1})	H_2 uptake (wt%, 1.0 bar, 77 K)	S content [a] (wt%)	Ref.
ThPOP-1	1050	2.23	0.39	This work
ThPOP-2	160	1.03	0.39	This work
SPT-CMP1	1631	1.72	0.08	S1
SPT-CMP2	1601	1.57	0.07	S1
SPT-CMP3	1334	1.34	0.04	S1
ThPOP-4	681	0.96	0.20	S2
ThPOP-5	810	1.07	0.20	S2
SPOP-9	860	1.43	0.13	S3
P-2	1222	1.66	0.05	S4

[a] Calculated sulfur elemental analysis.

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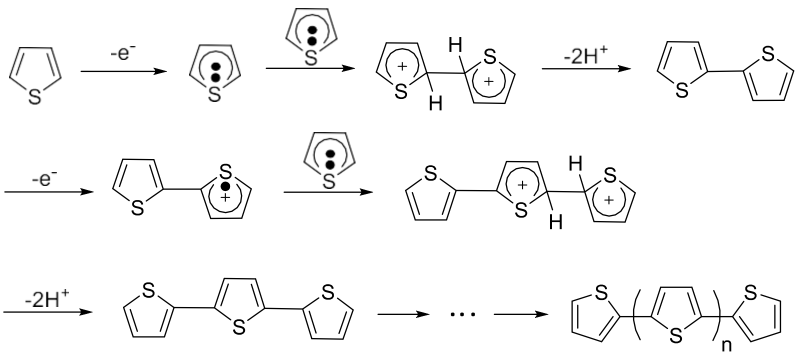

Scheme S1. The possible mechanism of oxidative polymerization of thiophene via coupling.

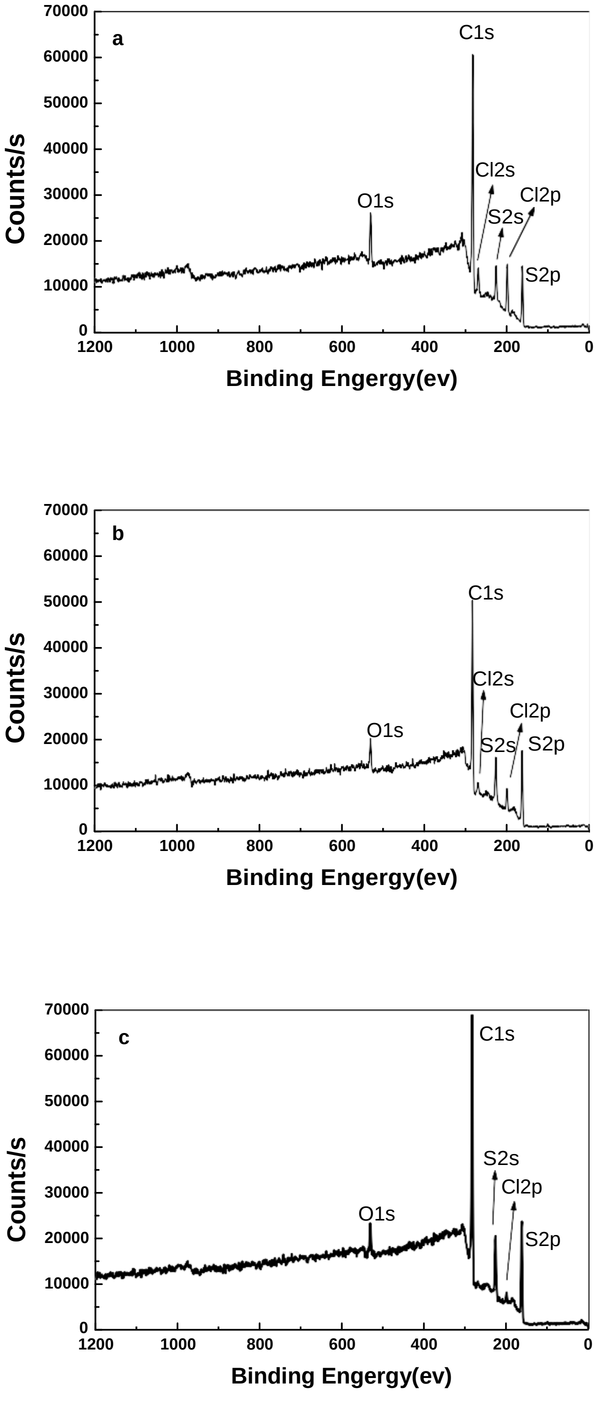

Fig. S1 XPS of **ThPOP-1** generated from different molar ratio of ferric chloride and single reaction site of **COTh**. The molar ratios of ferric chloride and single reaction site of **COTh** are (a) 5.0:1, (b) 2.0:1, and (c) 1.2:1, respectively.

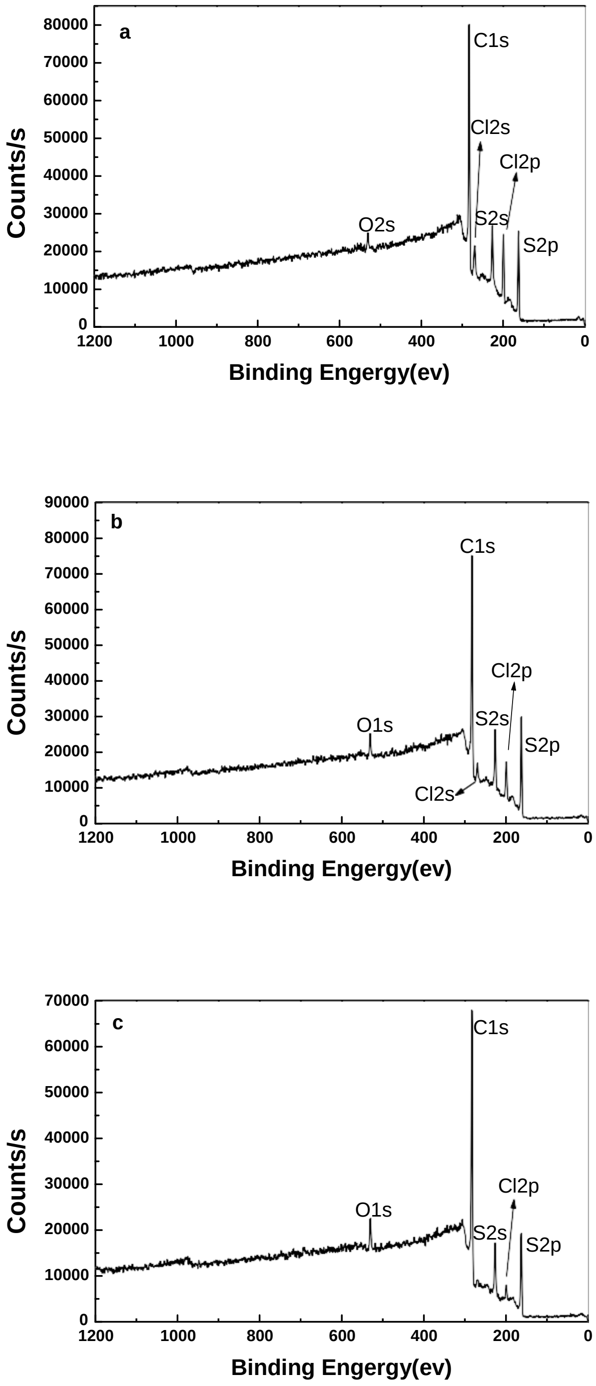

Fig. S2. XPS of **ThPOP-2** generated from different molar ratio of ferric chloride and single reaction site of **BTTh**. The molar ratio of ferric chloride and single reaction site of **BTTh** are (a) 5.0:1, (b) 2.0:1, and (c) 1.2:1, respectively.

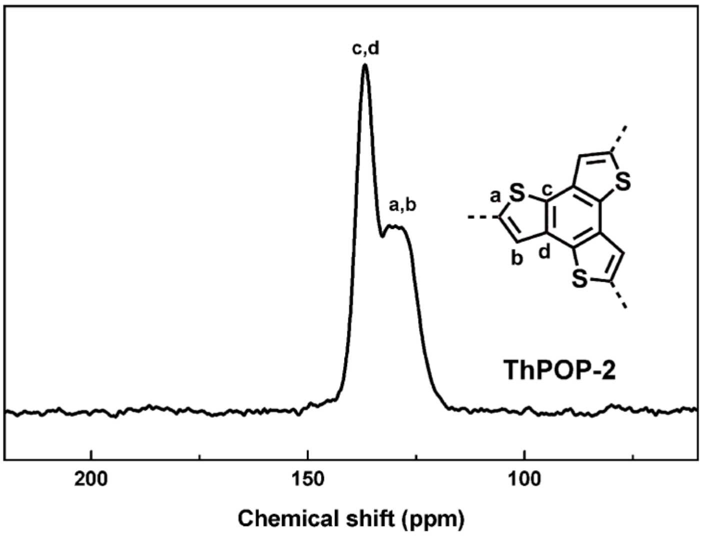

Fig. S3 Solid-state ^{13}C CP/MAS NMR spectra of **ThPOP-2**.

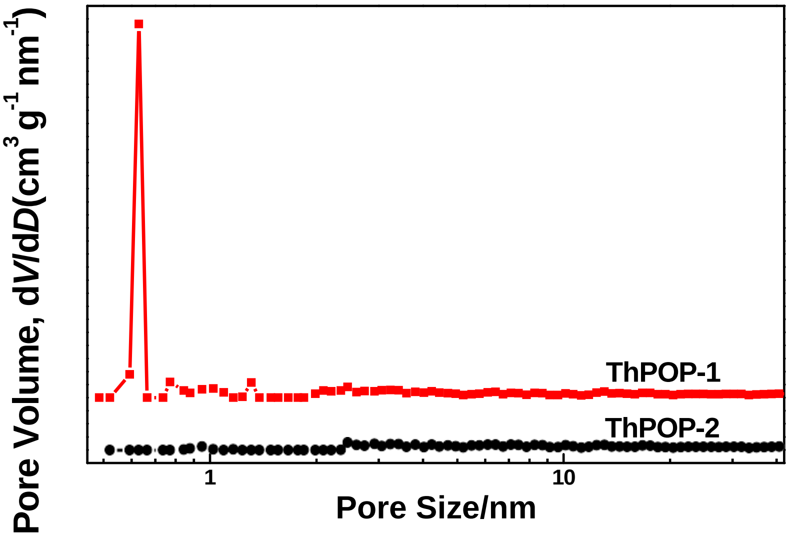

Fig. S4 PSD profiles of **ThPOP-1** (red) and **ThPOP-2** (black) calculated by the original NLDFT.