

## Supporting Information

# Direct arylation polymerization towards a narrow bandgap conjugated microporous polymer with hierarchical porosity

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## Experimental Section

### Measurements and Characterization.

Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Diamond TGA/DTA, at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from 30 to  $800\text{ }^{\circ}\text{C}$  under a nitrogen atmosphere. Fourier transform infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer. KBr-pellets were prepared by pressing a mixture of a very small amount of **DTP-CMP** polymer and KBr.  $^1\text{H-NMR}$  spectra for the monomer and **DTP-CMP** polymer were acquired on Bruker AV 300 spectrometer with TMS as the internal reference and  $\text{C}_2\text{D}_2\text{Cl}_4$  as the solvent for the monomer at room temperature and **DTP-CMP** polymer (**CMP-NTU1**) dispersed in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $100\text{ }^{\circ}\text{C}$  and sonication for ca. 1 h before measurement. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar). UV-vis-NIR absorbance spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer for a translucent chloroform solution of **DTP-CMP** polymers prepared by sonication. Electrochemical measurements were conducted on a CHI006D electrochemical analyzer with a three-electrode system under nitrogen atmosphere in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy carbon, platinum, and Ag-wires were used as a working, counter, and pseudo-reference electrodes, respectively. The **DTP-CMP** polymer films for electrochemical measurements were coated on the surface of glassy carbon electrode together with Nafion as a binder. Powder X-ray diffraction (PXRD) data were collected at 30kV, 10 mA on a Bruker D2 Phaser XRD diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ) with a step size of  $0.200397^{\circ}$  /min over  $2\theta$  range of  $5^{\circ} - 80^{\circ}$  at room temperature. The scanning electron microscopy images were obtained on a JEOL JSM 6390LA SEM microscope (JEOL), operating at an acceleration voltage of 30 kV. Metal Pt sputtering of the samples was

necessary. Gas sorption analyses were conducted using Quantachrome Instruments Autosorb-6 with extra-high pure gases.

### **Theoretical calculations**

Calculations were performed with Gaussian 09 using GaussView 5 to generate structures. Ground state geometry optimizations for both the monomer and conjugated microporous polymers model structure (**DTP-CMP**) was performed at the B3LYP level of theory with the 6-31+G(d) basis set.

**Materials.** Unless stated otherwise, starting materials and anhydrous solvents were obtained from Sigma-Aldrich and used without further purification. Compound **3** and **DBDTP** was prepared according reported procedures.[1, 2]All the reactions were carried out under N<sub>2</sub> atmosphere.

### **Synthetic Protocol**

**3,6-dibromobenzene-1,2-diamine.** To 150-ml round bottomed flask containing stir bar 4,7-dibromobenzo[c][1,2,5]thiadiazole, and Compound **1** (2 g, 6.8 mmol) was dissolved in 60 ml of anhydrous ethanol under nitrogen atmosphere and then cooled to 0 °C with ice bath followed by portionwise addition of NaBH<sub>4</sub>. The reaction mixture was stirred for 6 hr at room temperature and then poured to a flask containing water followed by extraction with diethyl ether (3X), the combined organic phase was washed with brine (2X), and drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The white solid were collected by filtration and used without further purification (1.38 g, 76 %).

**8,11-dibromodithieno[3,2-a:2',3'-c]phenazine, DBDTP.** To a 150 mL round bottomed flask containing stir bar diamine, Compounds **2** (1.38 g, 5.15 mmol) and diketone, Compound **3** (1.13 g, 5.15 mmol) was dissolved in ethanol (60 mL) and acetic acid (20 mL) under nitrogen atmosphere. After refluxing for 48 hrs, an orange precipitate was collected by filtration and washed with cold ethanol. Further purification *via* recrystallization in chloroform gave an orange solid (2

g, 86 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ) 8.56 (d, J = 3.12 Hz, 2H), 8.06 (s, 2H), 7.64 (d, J = 3.18 Hz, 2H).

**General synthetic protocol dithieno[3,2-a:2',3'-c]phenazine conjugated microporous organic polymer (DTP-CMP)**

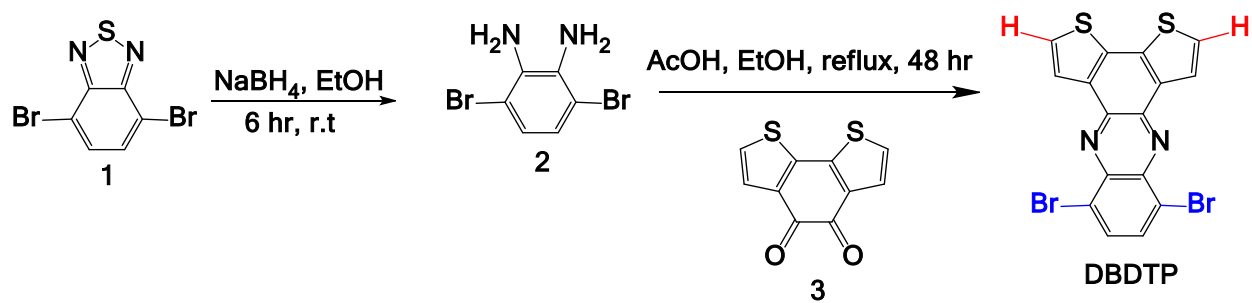
In a glove box, 8,11-dibromodithieno[3,2-a:2',3'-c]phenazine (135 mg, 0.3 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (7 mg, 5% mmol), (o-MeOPh)<sub>3</sub>P (6 mg, 10% mmol), K<sub>2</sub>CO<sub>3</sub>(104 mg, 0.75 mmol, 5 eq) , PivOH (8 mg, 0.5 eq) and solvent o-xylene (1.5 mL) were added in a microwave reaction vial with a magnetic stirring bar. The vial was sealed with a Teflon-lined cap and then removed from the glove box. The vial was heated in oil bath at different reaction temperature and time to afford a black precipitate, which was isolated by filtration followed by washing continuously with methanol, acetone, DMF, and acetone sequentially followed by Soxhlet washing with methanol, chloroform, and THF each for 24 hr. The black solid was subjected to overnight drying in a vacuum at 60 °C.

**CMP-NTU1** at 100 °C for 24 hr, Yield:110 mg, Anal.Calcd for C<sub>16</sub>H<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.73; H, 2.76; N, 9.58; S, 21.93. Found: C, 52.24; H, 1.08; N, 6.85; S, 16.00.

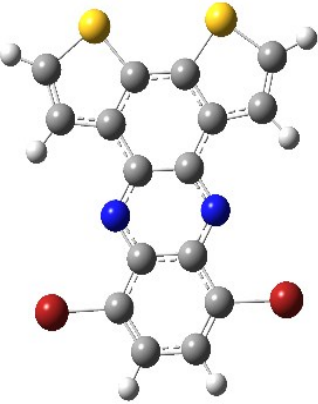
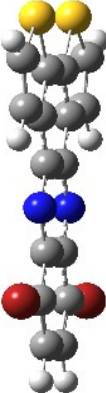
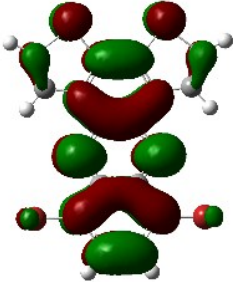
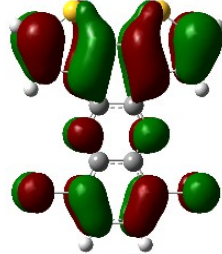
**CMP-NTU2** at 100 °C for 48 hr in, Yield:100 mg, Anal.Calcd for C<sub>16</sub>H<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.73; H, 2.76; N, 9.58; S, 21.93. Found: C, 51.18; H, 1.06; N, 6.65; S, 15.54.

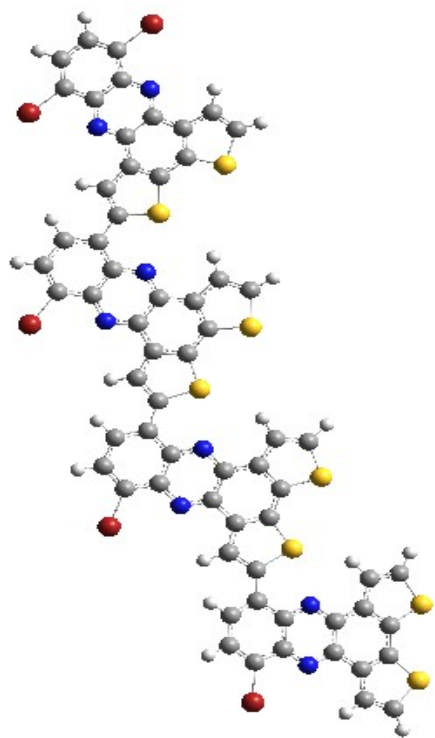
**CMP-NTU3** at 140 °C for 48 hr in, Yield:108 mg, Anal.Calcd for C<sub>16</sub>H<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.73; H, 2.76; N, 9.58; S, 21.93. Found: C, 58.71; H, 1.70; N, 6.57; S, 15.25.

**CMP-NTU4** at 140 °C for 7 days in, Yield:112 mg, Anal.Calcd for C<sub>16</sub>H<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.73; H, 2.76; N, 9.58; S, 21.93. Found: C, 61.17; H, 1.88; N, 6.86; S, 15.97.

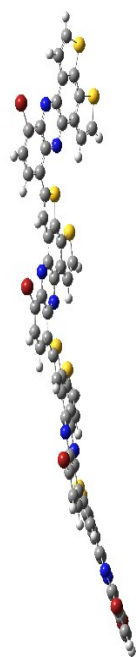


**Scheme S1.** Synthesis of 8,11-dibromodithieno[3,2-a:2',3'-c]phenazine, **DBDTP**

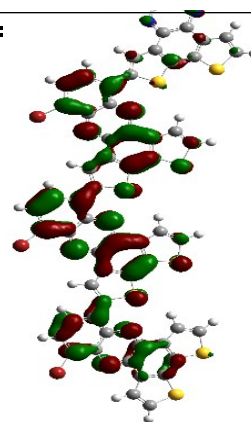
Optimized Geometry		Energy level and bandgap (eV)	<sup>1</sup> Gibbs free energy ( $\Delta G$ ) (kCal/mol of the monomer)
Top view	Side view		
 <p><b>Monomer - DBDTP</b></p>		<p><b>LUMO = -2.703</b></p> 	
		<p><b>HOMO = -5.891</b></p>  <p><b>Bandgap = 3.188</b></p>	



Linear- tetramer (L<sub>4</sub>)

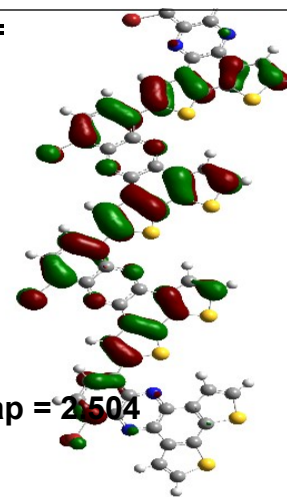


LUMO :

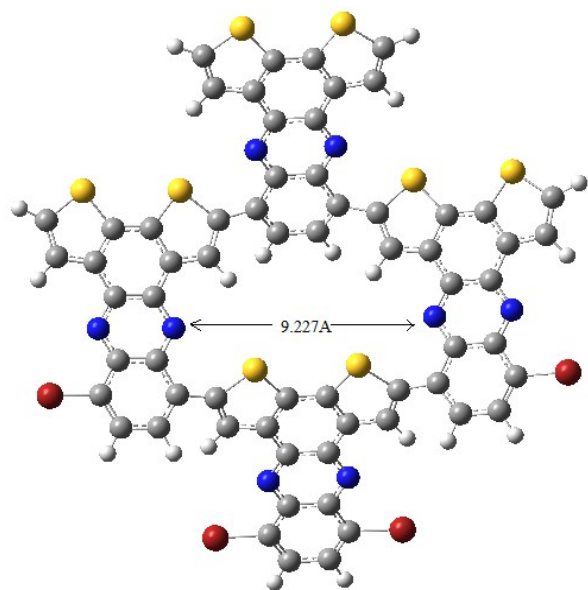


-3.609<sup>a</sup>

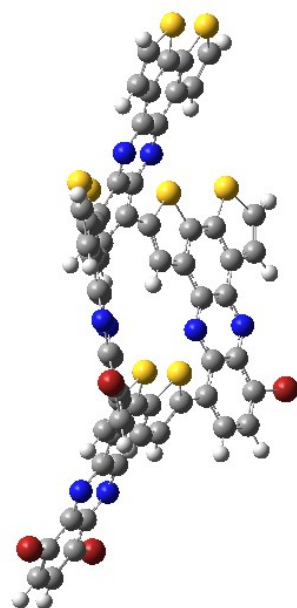
HOMO :



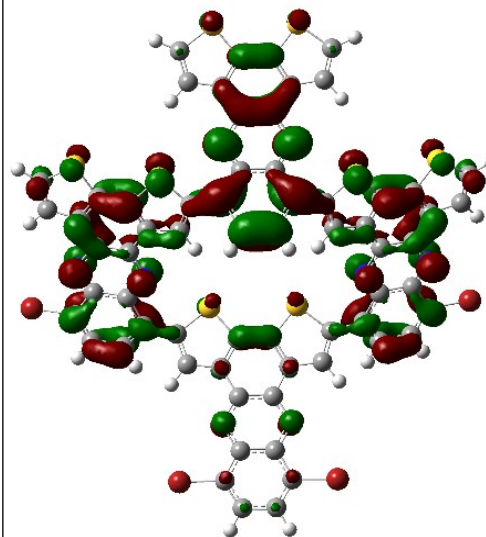
Bandgap = 2.504



Cyclic-tetramer (C<sub>4</sub>)

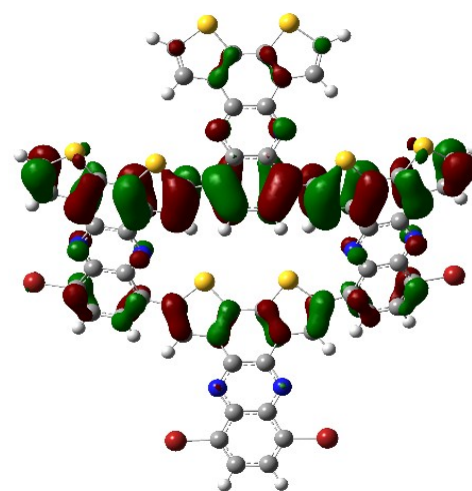


LUMO = -2.930



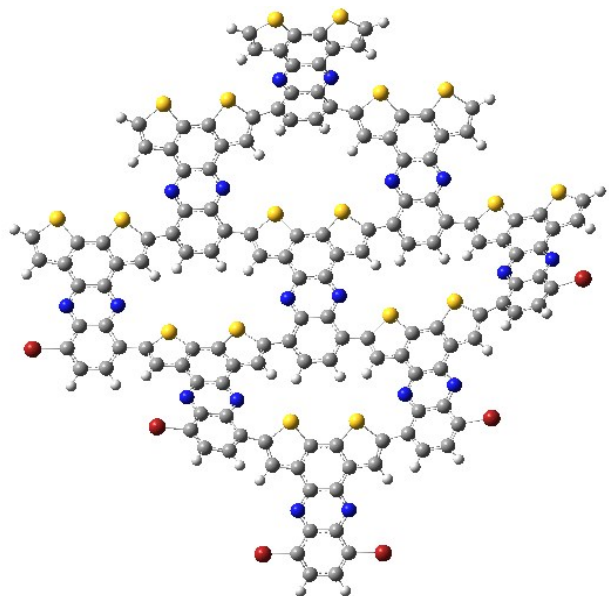
-4.243<sup>b</sup>

HOMO = -5.361

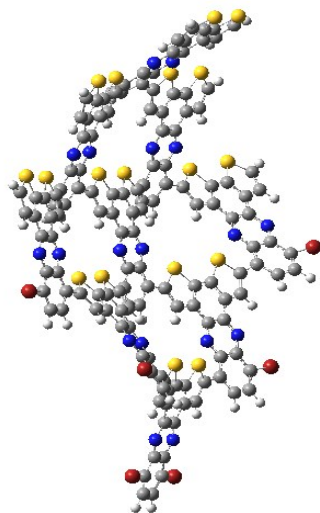


Bandgap = 2.431

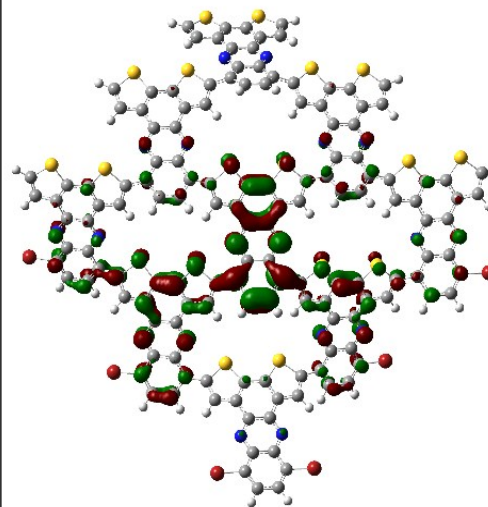




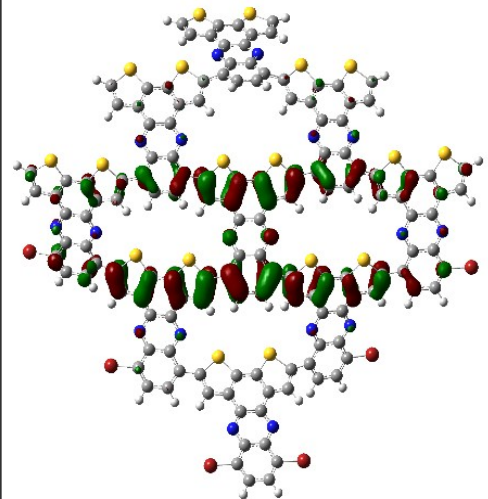
An extended conjugated microporous polymer (C<sub>9</sub>)



LUMO = -3.063



HOMO = -5.187



Bandgap = 2.124

-5.394 eV

<sup>1</sup>**Figure S1.** Representative geometry-optimized structure by DFT (BLYP 6-31G(d)) for **DBDTP** monomer, linear tetramer (**L<sub>4</sub>**), cyclic tetramer (**C<sub>4</sub>**), and an extended conjugated network (**C<sub>9</sub>**).

## <sup>1</sup>**Summary of DFT BLYP 6-31G(d) calculations**

- **Sum of electronic and thermal free energies at 140 °C (in Hartrees):**

1. Monomer (**DBDTP**): -6662.525214 Hartree
2. Microporous Polymer (**Cyclic-tetramer**): -16360.833762 Hartree
3. Linear Polymer (**linear-tetramer**): -18933.153254 Hartree
4. HBr: -2572.323535 Hartree

- **<sup>a</sup>Reaction 1:** 4 Monomers → Cyclic tetramer (**C<sub>4</sub>**) + 4 HBr

$$\begin{aligned}\Delta G_1 &= -16360.833762 + 4*(-2572.323535) - 4*(-6662.525214) \\ &= -0.027046 \text{ Hartree} = \mathbf{-16.972 \text{ kCal/mol}} \\ &= \mathbf{-4.243 \text{ kCal/mol per monomer}}\end{aligned}$$

- **<sup>b</sup>Reaction 2:** 4 Monomers → Linear tetramer (**L<sub>4</sub>**) + 3 HBr

$$\begin{aligned}\Delta G_2 &= -18933.153254 + 3*(-2572.323535) - 4*(-6662.525214) \\ &= -0.023003 \text{ Hartree} = \mathbf{-14.435 \text{ kCal/mol}} \\ &= \mathbf{-3.609 \text{ kCal/mol per monomer}}\end{aligned}$$

- **<sup>c</sup>Reaction 3:** 9 Monomers → Cyclic polymer (**C<sub>9</sub>**) + 12 HBr

$$\begin{aligned}\Delta G_3 &= -29094.921870 + 12*(-2572.323535) - 9*(-6662.525214) \\ &= -0.077364 \text{ Hartree} = \mathbf{-48.5466 \text{ kCal/mol}}\end{aligned}$$

= -5.394 kCal/mol per monomer

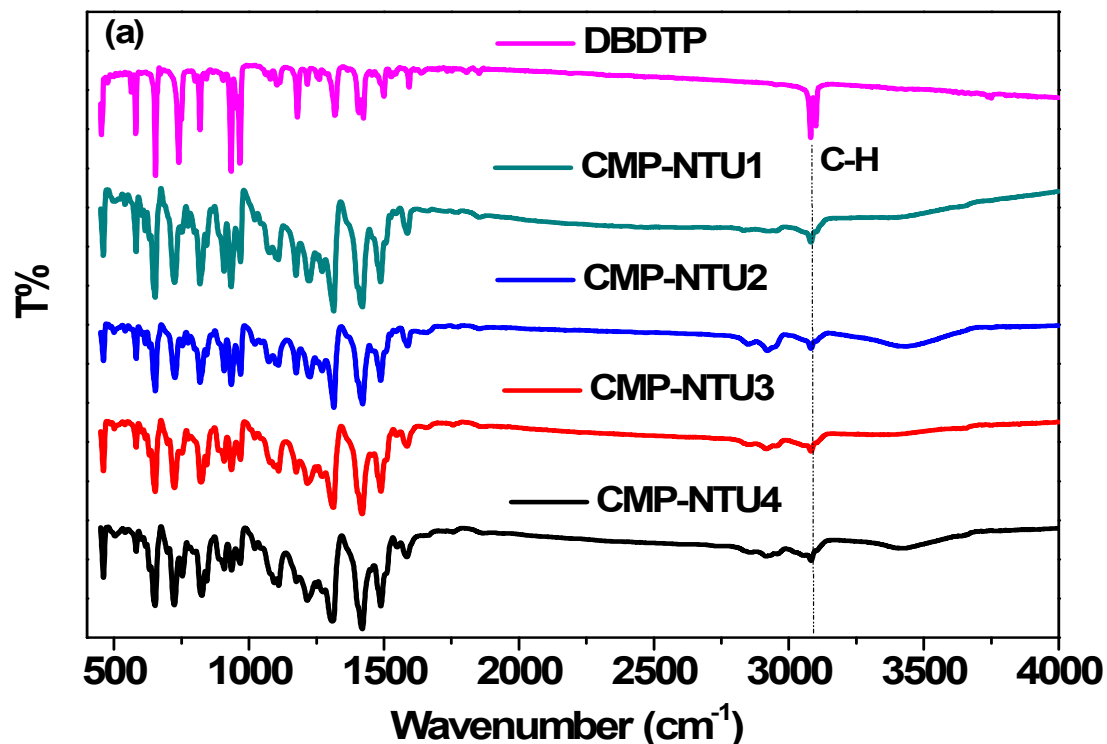
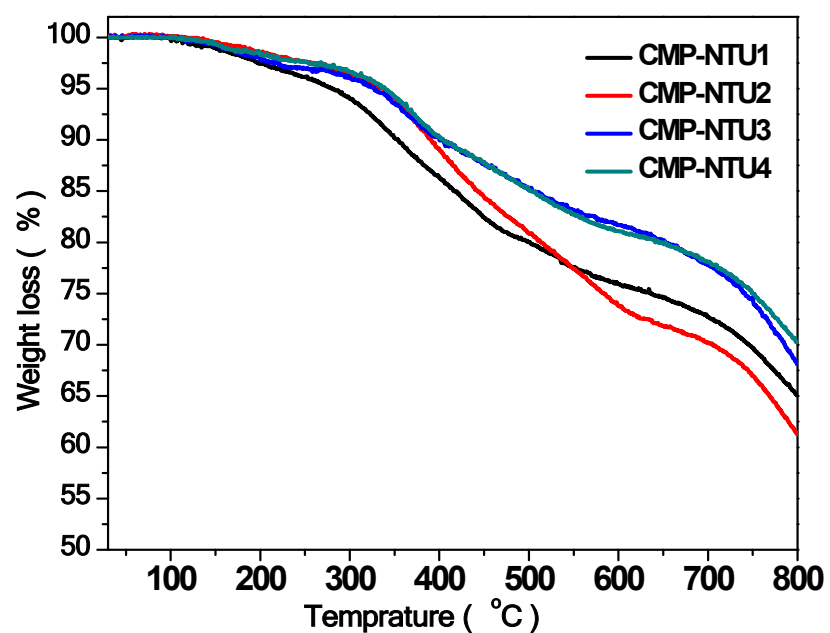


Figure S2. FT-IR spectra of DTP-CMP.

Table S1. Peak assignments for FT-IR spectrum of DTP-CMP.

Peak (cm <sup>-1</sup> )	Assignment and Note
3000-3100 cm <sup>-1</sup>	Aromatic C-H stretch
1558-1615 cm <sup>-1</sup>	C=N stretching of the imine
1456-1527 cm <sup>-1</sup>	C=C stretch in typical region for fused aromatics

<i>1345-1461 cm<sup>-1</sup></i>	C=C vibrational modes for <b>DBDTP</b> building block
<i>1281-1345 cm<sup>-1</sup></i>	C=C vibrational mode of benzene
<i>1054-1135 cm<sup>-1</sup></i>	C-N stretching
<i>805-868 cm<sup>-1</sup>, 651 cm<sup>-1</sup></i>	C-H out of plane bands for p-substituted aromatic
<i>1180 cm<sup>-1</sup></i>	Asymmetric C-Br
<i>580 cm<sup>-1</sup></i>	Symmetric C-Br



**Figure S3.** TGA plots of **DTP-CMP** polymers with a heating rate of 10 °C min<sup>-1</sup> under nitrogen.

**Table S2.** Electrochemical properties of **DTP-CMP** polymers

<b>DTP-CMP</b>	<b>E<sub>ox</sub><sup>onset</sup></b>	<b>E<sub>red</sub><sup>onset</sup></b>	<b><sup>a</sup>HOMO<sup>elc</sup></b>	<b><sup>a</sup>LUMO<sup>elc</sup></b>	<b><sup>b</sup>E<sub>g</sub><sup>elc</sup></b>
	(V)	(V)	(eV)	(eV)	(eV)

CMP-NTU1	1.2	-0.3	-5.4	-3.9	1.5
CMP-NTU2	1.2	-0.2	-5.4	-4.0	1.4
CMP-NTU3	1.2	-0.3	-5.4	-3.9	1.5
CMP-NTU4	1.2	-0.3	-5.4	-3.9	1.5

<sup>a</sup> $HOMO^{ele}/LUMO^{ele} = -(4.8 - E_{1/2, Fc, Fc^+} + E_{ox/red, onset})$ .  $E_{1/2, Fc, Fc^+} = (E_{ap} + E_{cp})/2 = 0.63 V$ . <sup>b</sup> $E_g^{ele} = E_{LUMO}^{ele} - E_{HOMO}^{ele}$ .

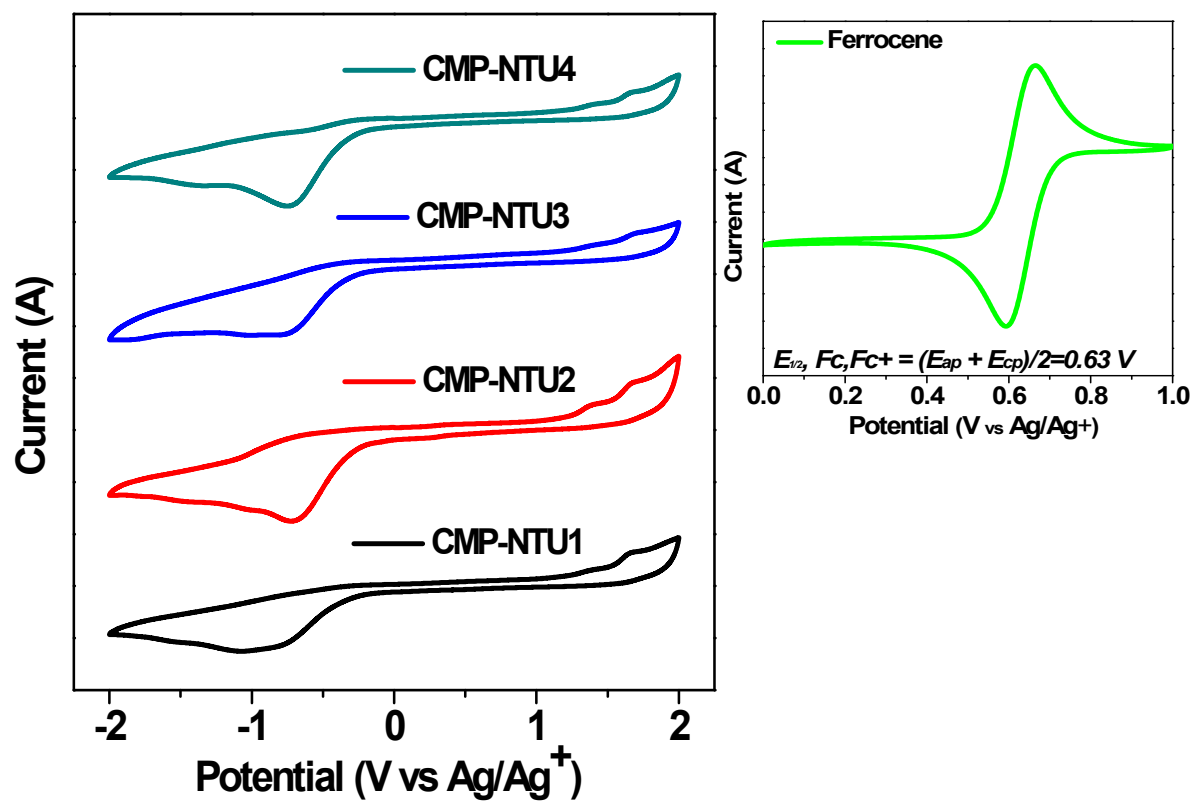


Figure S4. Cyclic voltammograms of DTP-CMP polymers.

Table S3. Porosity of DTP-CMP polymers

Entry	BET/Langmuir surface area (m <sup>2</sup> /g)	Pore diameter (Å)	Pore volume (cc/g)
CMP-NTU1	70/525	8.79	0.34
CMP-NTU2	87/684	8.68	0.45
CMP-NTU3	160/864	17.72	0.60
CMP-NTU4	175/892	12.01	0.70

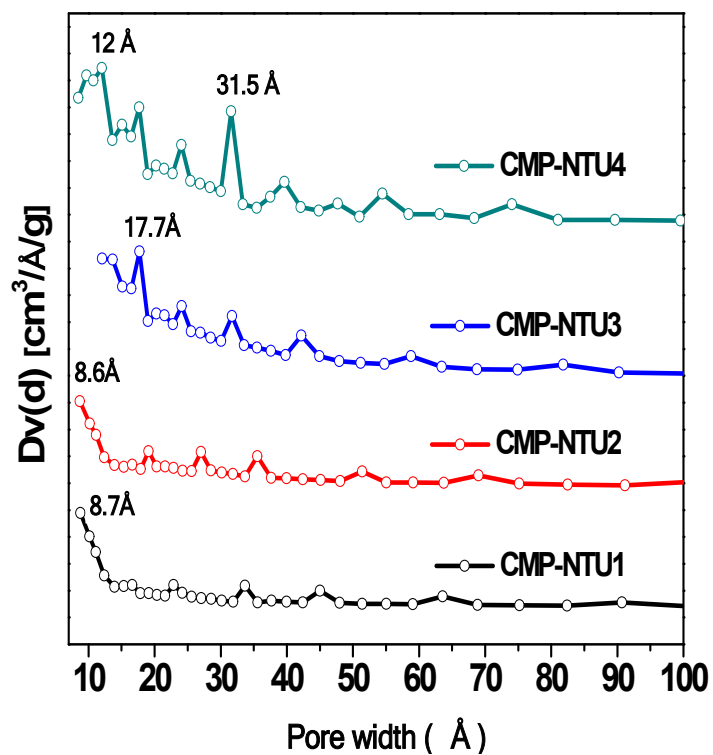
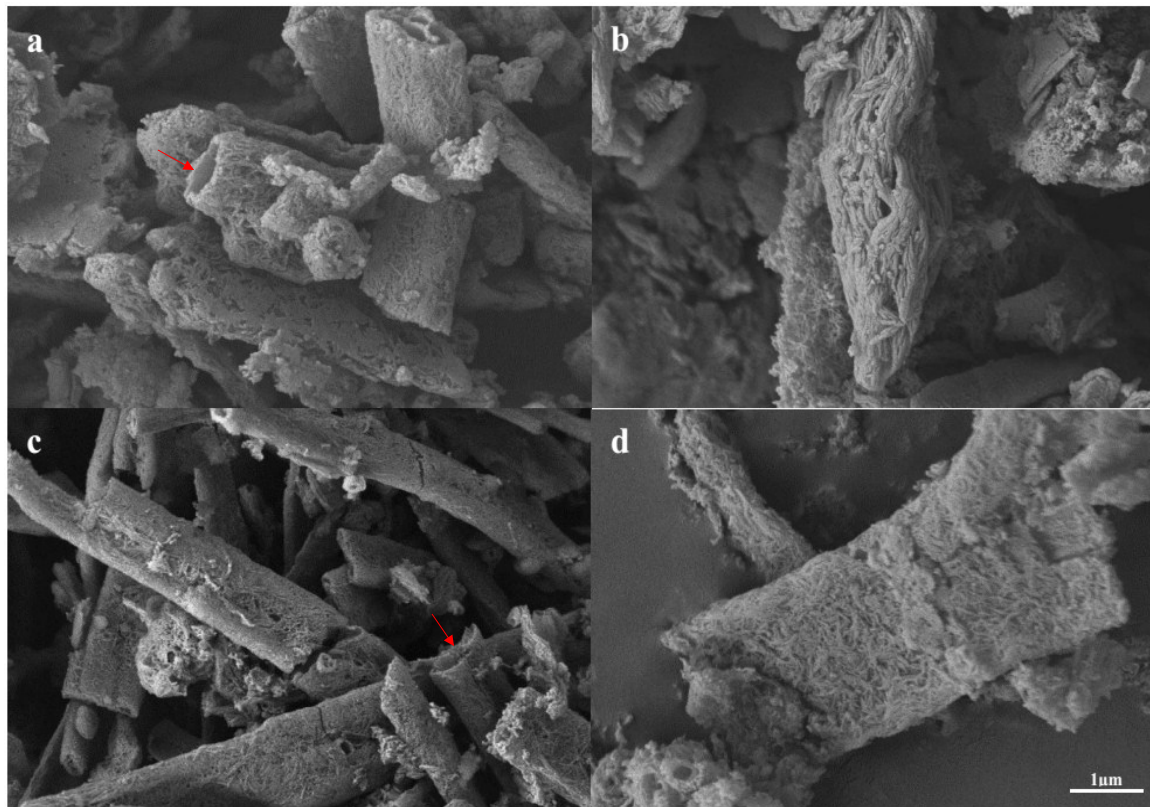
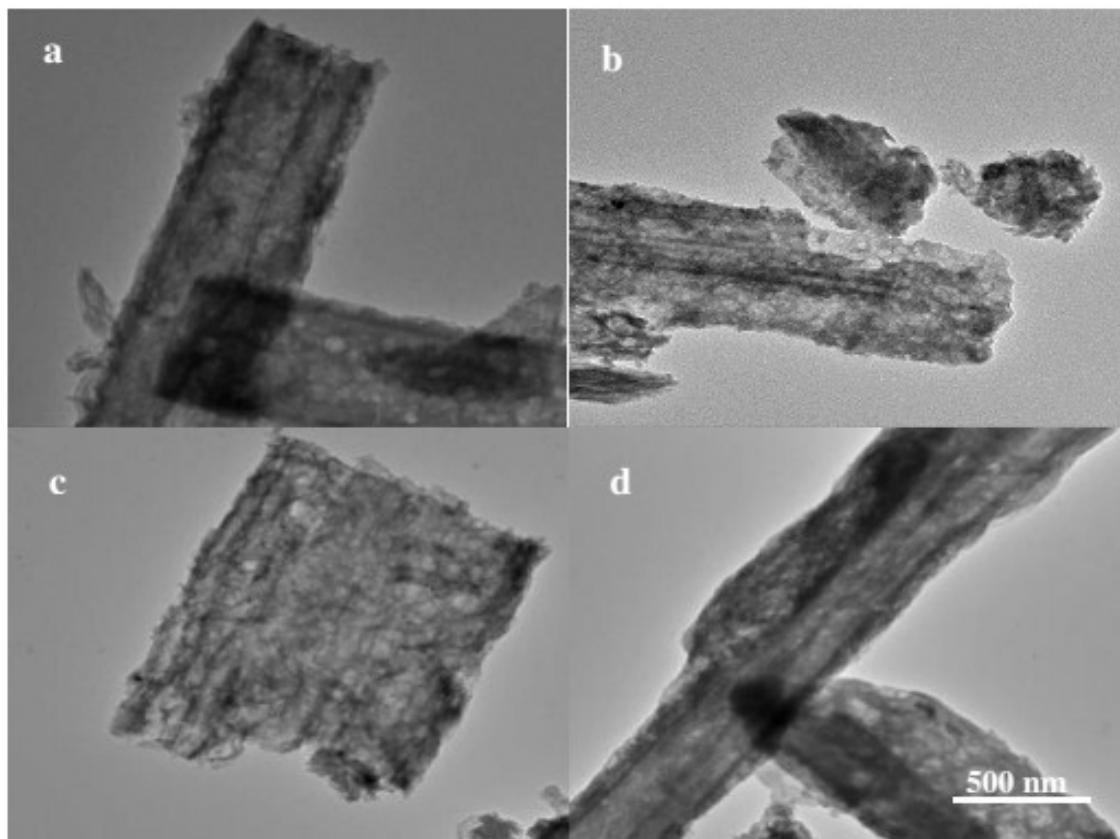


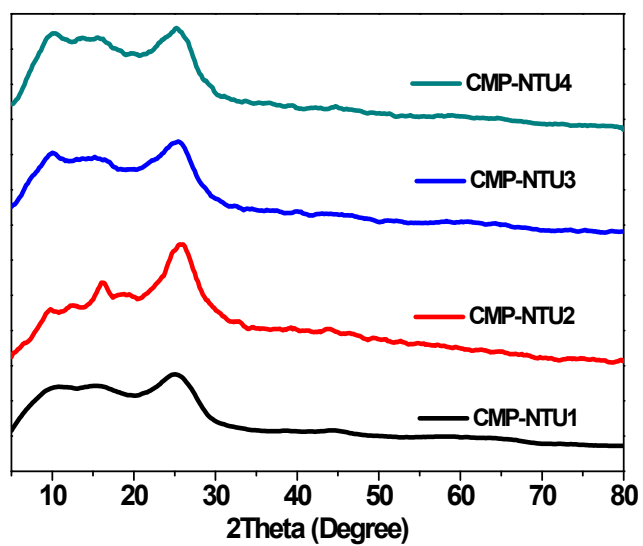
Figure S5. Pore size distribution profiles for DTP-CMP porous polymers.



**Figure S6.** SEM images for CMP-NTU1 (a), CMP-NTU2 (b), CMP-NTU3 (c), and CMP-4 (d). Red arrows indicate the tube-like structures of CMPs.

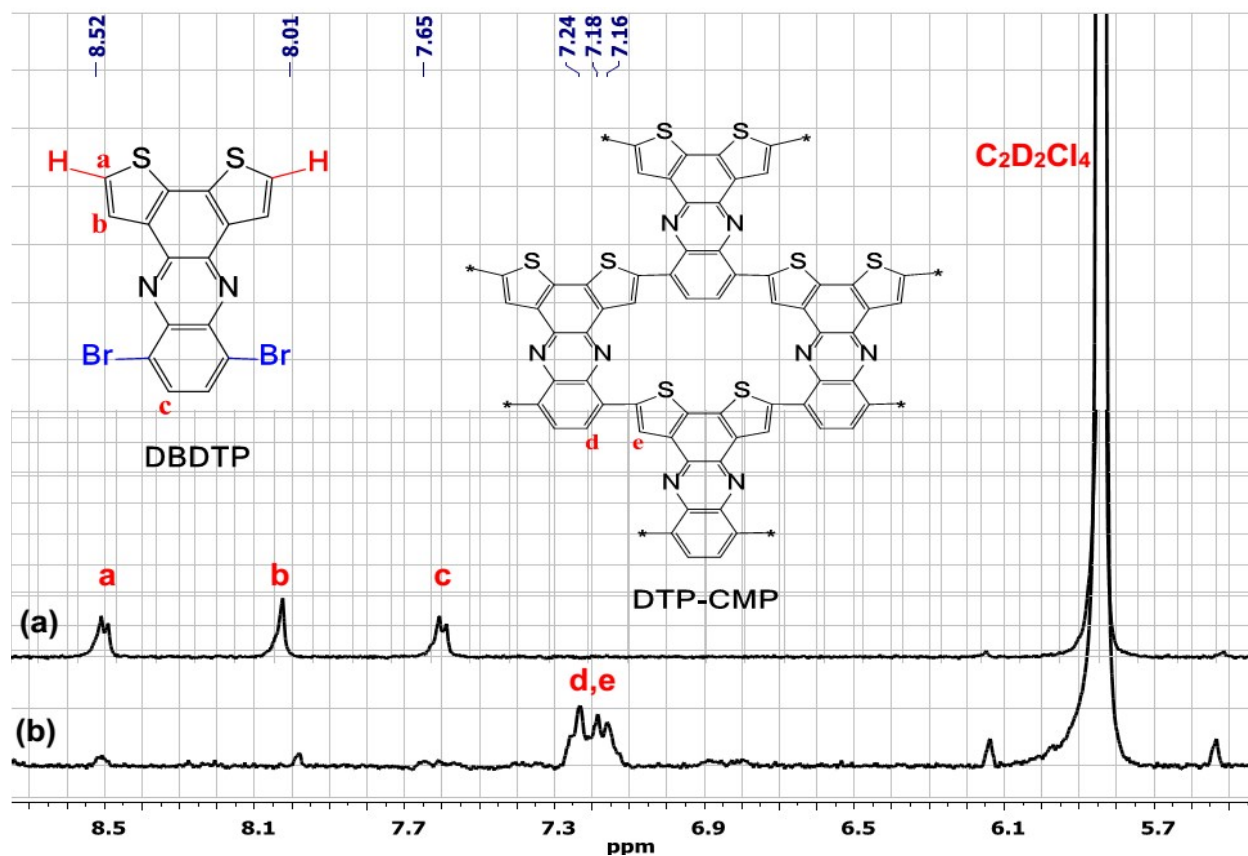


**Figure S7.** TEM images for DTP-CMP for CMP-NTU1 (a), CMP-NTU2 (b), CMP-NTU3 (c), and CMP-NTU4 (d).



**Figure S8.** PXRD spectra for DTP-CMP.





**Figure S9.**  $^1\text{H}$  NMR spectra (a) **DBDTP** monomer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at r.t., and (b) **CMP-NTU1** dispersed in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 100 °C.

## REFERENCES

1. Arroyave, F.A., C.A. Richard, and J.R. Reynolds, *Efficient Synthesis of Benzo [1, 2-b: 6, 5-b'] dithiophene-4, 5-dione (BDTD) and Its Chemical Transformations into Precursors for  $\pi$ -Conjugated Materials*. *Organic letters*, 2012. **14**(24): p. 6138-6141.
2. Gao, X., et al., *A Straightforward Synthesis of Chlorine-Bearing Donor–Acceptor Alternating Copolymers with Deep Frontier Orbital Levels*. *Macromolecular Chemistry and Physics*, 2014. **215**(14): p. 1388-1395.