

Electronic Supplementary Information for
**Enhanced Redox activity of hollow conjugated microporous polymer
through a generation of carbonyl groups by the carbonylative Sonogashira coupling**

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Experimental Sections

Transmission (TEM) and scanning electron microscopy (SEM) were conducted using a JEOL 2100F and a FE-SEM (JSM6700F). N₂ adsorption-desorption isotherm curves were obtained using a BELSORP II-mini analyzer. The pore size distribution diagrams were obtained based on the density functional theory (DFT). Infrared absorption spectroscopy was conducted using a Bruker VERTEX 70 FT-IR spectrometer. Solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy was conducted using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities of Seoul National University. A 4 mm magic angle spinning probe was used with a spinning rate of 5 kHz. Powder X-ray diffraction (PXRD) studies were conducted using a Rigaku MAX-2200 (filtered Cu-Kα radiation). Cyclic voltammetry (CV) on the model compounds was conducted using a CH1600C potentiometer. Thermogravimetric analysis (TGA) was conducted using a Seiko Exstar 7300. Elemental analysis was conducted using a CE EA1110 analyzer.

Electrochemical studies on model compounds (Fig. 1 in the text)

1,4-Bis(2-phenylethynyl)benzene was purchased from Aldrich. Co and was used as received. 1,4-Bis(3-phenylpropynoyl)benzene is a known compound and was prepared by the synthetic procedure in the literature.¹ In our study, the following procedures were applied. Terephthaloyl chloride (1.0 g, 4.9 mmol), (PPh₃)₂PdCl₂ (69 mg, 98 μmol), CuI (37 mg, 20 μmol), triethylamine (5 mL), toluene (5 mL), and phenyl acetylene (0.65 mL, 6.8 mmol) were added to a 50 mL two-neck Schlenk flask. The reaction mixture was heated at 110°C for 2.5 hours. After being cooled to room temperature, the product was extracted with a methylene chloride and brine solution. After drying with MgSO₄, the solvent was removed by a rotary evaporator. The product was separated by column chromatography using a 9:1 mixture of hexane and ethyl acetate as eluent. For the electrochemical studies shown in Fig. 1 in the text, 5 mM model compounds and ferrocene solutions in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile were used. Working, counter, and reference electrodes were carbon, Pt wire, and Ag/AgNO₃, respectively. The scan rate was 100 mV/s.

Synthetic procedure for H-CMP and H-CMP-BPPB

Silica spheres with an average diameter of 173 ± 9 nm were prepared by the Stöber method in the literature.² In our work, the following procedures were applied. Distilled water (8 mL), ethanol (200 mL), and ammonia solution (28~30%, 5 mL) were added to a 500 mL Erlenmeyer flask. After the mixture was stirred at room temperature for 30 mins, tetraethyl orthosilicate (TEOS, 14 mL, 0.072 mol) was added. The mixture was stirred at room temperature for 18 hours. The silica spheres were separated by centrifugation, washed with a 1:1:1 mixture of acetone, methylene chloride, and hexane three times, and dried under vacuum. For the preparation of H-CMP, silica spheres (0.30 g), $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 20 μmol), CuI (2 mg, 11 μmol), toluene (15 mL), and triethylamine (15 mL) were added to a flame-dried 50 mL two-neck Schlenk flask under argon. After the mixture was treated with sonication for 1 hour, 1,3,5-triethynylbenzene (30 mg, 0.20 mmol) and 1,4-diiodobenzene (99 mg, 0.30 mmol) were added. The reaction mixture was heated at 90°C for 48 hours. After being cooled to room temperature, the powder $\text{SiO}_2\text{@CMP}$ was separated by centrifugation, washed with a 1:1 mixture of methylene chloride and methanol five times, and dried under vacuum. $\text{SiO}_2\text{@CMP}$ (~0.35 g) was added to a 50 mL Falcon tube. After a mixture of HF solution (7.5 mL), methanol (20 mL), and water (15 mL) was added, the reaction mixture was stirred at room temperature for 2 h. *Caution: the HF solution is extremely dangerous and should be handled with special gloves in the hood.* The resultant H-CMP was retrieved by centrifugation, washed with a mixture of methanol (20 mL) and water (20 mL) five times and then, with acetone (40 mL) three times. and dried under vacuum. *Caution: The excess HF retrieved from the reaction mixture during the work up processes should be neutralized by addition to 3 M NaOH solution.*

For the preparation of H-CMP-BPPB, silica spheres (0.30 g), $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 20 μmol), CuI (2 mg, 11 μmol), toluene (15 mL), and triethylamine (15 mL) were added to a flame-dried 50 mL two-neck Schlenk flask under argon. After the mixture was treated with sonication for 1 hour, 1,3,5-triethynylbenzene (30 mg, 0.20 mmol) and 1,4-diiodobenzene (99 mg, 0.30 mmol) were added. The amounts of building blocks were optimized. It is noteworthy that when the amounts of 1,3,5-triethynylbenzene and 1,4-diiodobenzene were increased by two times, irregular CMP powder was significantly mixed. The reaction mixture was bubbled with carbon monoxide. The reaction mixture was heated at 90°C for 48 hours under carbon monoxide (CO balloon). After being cooled to room temperature, the solid ($\text{SiO}_2\text{@CMP-BPPB}$) was separated by centrifugation, washed with a 1:1 mixture of methylene chloride and methanol five times, and dried under vacuum. $\text{SiO}_2\text{@CMP-BPPB}$ (~0.35 g) was added to a 50 mL Falcon tube. After a mixture of HF solution (7.5 mL), methanol (20 mL), and water (15 mL) was added, the reaction mixture was stirred at room temperature for 2 h. *Caution: the HF solution is extremely dangerous and should be handled with special gloves in the well-ventilated hood.* The resultant H-CMP-BPPB was retrieved by centrifugation, washed with a mixture of methanol (20 mL) and water (20 mL) five times and then, acetone (40 mL) three times, and dried under vacuum. *Caution: The excess HF retrieved from reaction mixture during the work up processes should be neutralized by addition to 3 M NaOH solution.*

Experimental procedures for electrochemical studies

For the fabrication of working electrodes, the electrode materials, H-CMP or H-CMP-BPPB (35 mg), Super P carbon black (50 mg), and polyvinylidene fluoride (PVDF, 15 mg, 115 mg of 13% PVDF in NMP), and 1-methyl-2-pyrrolidinone (NMP, 200 mg) were mixed using a mortar and a pestle. The resultant slurry was coated to Ti foil (0.127 mm thick, Alfa Aesar, areal size of 0.87 cm × 0.77 cm using a spatula and dried in an oven at 80°C for 1 hour and in a vacuum oven at 110°C overnight. The loading amount of active materials was calculated ~1.04 mg/cm². Two working electrodes were prepared for the fabrication of a symmetric coin cell type supercapacitor.

For the fabrication of symmetric coin cell type supercapacitor, one working electrode was located on the CR2032 cap. Two drops (~80 mg) of 1 M H₂SO₄ aqueous electrolyte were loaded on the working electrode. After separator (circular shape with a diameter of 1.9 cm, Hyundai Micro, No. 20 filter paper, HD20 MN. 020, 5~ 8 μm) was loaded, two drops (~80 mg) of 1 M H₂SO₄ aqueous electrolyte were loaded. The other working electrode was loaded (the electrode materials in the direction to separator). 1T sus space disk, a circular spring, CR2032 cap were loaded. Using a crimper, the CR2032 type coin cell supercapacitor was assembled. After the cells standing for 24 hours, the electrochemical studies were conducted using an electrochemical workstation (WonAtech ZIVE SP1). The scanned voltage range was +0.5 ~ -0.5 V. When we used the 6 M KOH as electrolyte instead of 1 M H₂SO₄, gas was significantly generated to result in disassembly of the cells due to the chemical reaction of electrolyte with electrode materials. The cell capacitances (C_{cell}) were obtained from the slope ($\Delta V/\Delta t$) of discharge curves by the following equation; $C_{\text{cell}} = I/[(\Delta V/\Delta t)m]$, where I is the applied current (A), $\Delta V/\Delta t$ is the slope of discharge curves after a IR drop at the beginning of the discharge curve, and m is the total mass of electrode materials in both working electrodes (g). The specific capacitance (C_s) of the single electrode was obtained by the following equation; $C_s = 4C_{\text{cell}}$.³

References

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Fig. S1 Cyclic voltammograms of symmetric coin cell type pseudocapacitors (electrolyte: 1 M H₂SO₄) of H-CMP-BPPB and H-CMP.

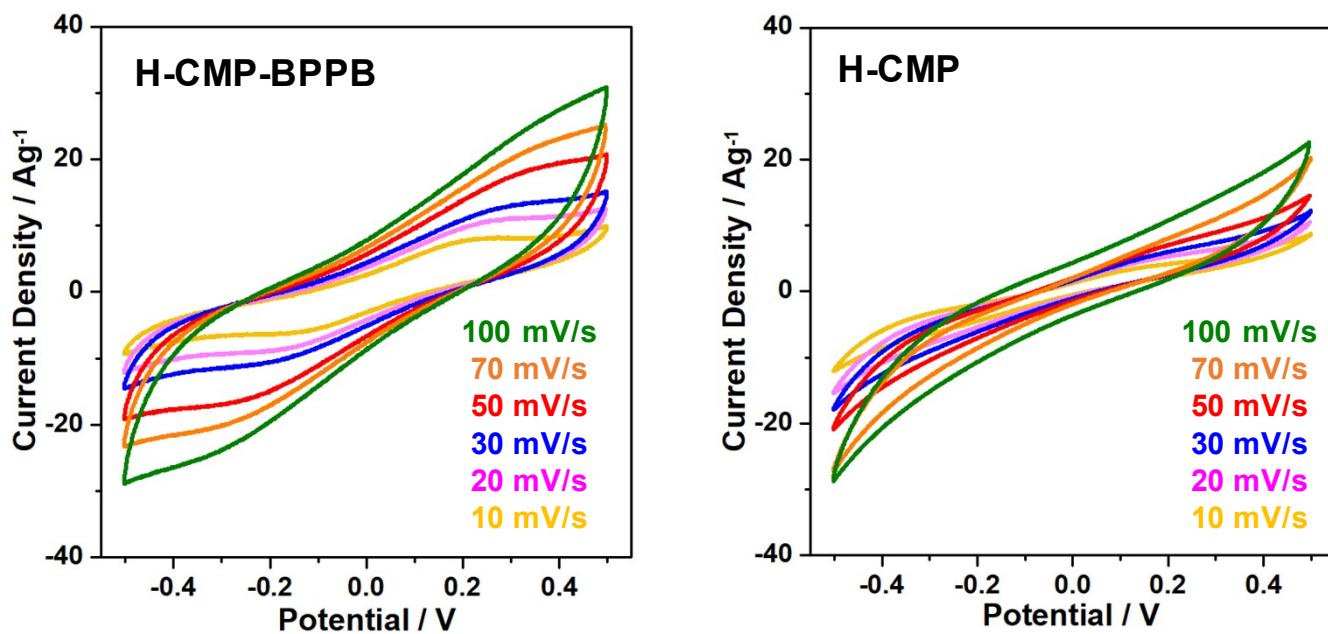


Fig. S2 TEM images of H-CMP and H-CMP-BPPB retrieved after 10000 cycling.

