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Electronic Supplementary Information for Hollow and microporous triphenylamine networks post-modified with TCNE for enhanced organocathode performance

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Experimental Sections

Transmission (TEM) and scanning electron microscopy (SEM) images were obtained using a JEOL 2100F unit and a FE-SEM (JSM6700F), respectively. The N₂ adsorption-desorption isotherms were measured at 77K using a BELSORP II-mini equipment. The pore size analysis was conducted based on the DFT method. PXRD patterns were obtained using a Rigaku MAX-2200 (filtered Cu-Ka radiation). Infrared absorption spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. The solid phase ¹³C-NMR spectroscopy (CPTOSS) was conducted using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University utilizing a 4 mm magic angle spinning probe. The spinning rate was 5 kHz. ¹H and ¹³C NMR spectra were obtained by 400 MHz and 500 MHz Varian spectrometers. Elemental analysis was conducted using a CE EA1110 instrument. The electrochemical studies were conducted using a WBCS3000 automatic battery cycler system.

Synthetic procedure for H-MTPN

Tris(4-iodophenyl)amine was prepared by the synthetic procedure in the literature.¹ In our work, triphenylamine (1.5 g, 6.1 mmol), N-iodosuccinimde (4.4 g, 20 mmol), and methylene chloride (50 mL) were added to a flame dried 100 mL Schlenk flask. The glassware was coated with an Al foil. After acetic acid (20 mL) being added, the reaction mixture was stirred at room temperature overnight. The solution was treated with sodium thiosulfate and brine solution and dried using Na_2SO_4 . The product was separated by column chromatography using a 9:1 mixture of hexane and methylene chloride as eluent and further purified by recrystallization in methanol.

Tris(4-ethynylphenyl)amine was prepared by the synthetic procedures in the literature.² In our work, tri(4iodophenyl)amine (3.3 g, 5.3 mmol), trimethylsilylacetylene (4.4 mL, 32 mmol), (PPh₃)₂PdCl₂ (0.22 g, 0.32 mmol), CuI (40 mg, 0.21 mmol), triphenylphosphine (0.17 g, 0.64 mmol), diethylamine (20 mL), and THF (30 mL) were added to a flame dried 100 mL Schlenk flask. The reaction mixture was heated at 80 °C overnight. After being cooled to room temperature, the solvent was removed by evaporation. The product was extracted with methylene chloride and water. After drying with MgSO₄, the solvent was removed by evaporation. The product was separated by column chromatography using a 9:1 mixture of hexane and methylene chloride as an eluent and further purified by recrystallization in methanol. Tris(4-trimethylsilylethynylphenyl)amine (1.2 g, 2.3 mmol) was dissolved in methylene chloride (50 mL). NaOH (0.35 g, 8.8 mmol) dissolved in methanol (10 mL) was added to the solution. After stirring at room temperature for 3 h, the solvent was removed by evaporation. The product was extracted using methylene chloride and brine. After drying with $MgSO_4$, the solvent was evaporated. The product was separated by column chromatography using an 8:1 mixture of hexane and methylene chloride as an eluent. The product, tris(4-ethynylphenyl)amine was further purified by recrystallization in methanol.

ZIF-8 nanoparticles were prepared by the synthetic procedure in the literature.³ In our work, for the preparation of ZIF-8 nanoparticles with an average size of 128 ± 13 nm, zinc nitrate hexahydrate (30 g, 0.10 mol) was dissolved in methanol (100 mL). Hexadecyltrimethylammonium bromide (CTAB, 1.8 g, 5.0 mmol) was dissolved in methanol (25 mL). 2-Methylimidazole (6.6 g, 80 mmol) was dissolved in methanol (100 mL). Zinc nitrate solution, CTAB solution, and then, 2-methylimidazole solution were added to a glass bottle. The reaction mixture was held for 18 h without stirring at room temperature. The resultant ZIF-8 nanoparticles were separated by centrifugation, washed with methanol, and dried under vacuum.

To prepare the ZIF-8@MTPN, a flame-dried 100 mL Schlenk flask was charged with argon. ZIF-8 particles (0.40 g), Pd(PPh₃)₂Cl₂ (17 mg, 0.024 mmol), and CuI (4.6 mg, 0.024 mmol) were added to THF (10 mL) in a flame-dried 100 mL Schlenk flask. Tris(4-ethynylphenyl)amine (76 mg, 0.24 mmol) and tris(4-iodophenyl)amine (0.15 g, 0.24 mmol) were dissolved in THF (10 mL) and added to the reaction mixture. After triethylamine (40 mL) being added, the reaction mixture was heated at 90 °C for 2 days. After being cooled to room temperature, the powder was retrieved by centrifugation, washed with methylene chloride, methanol, and acetone, and dried under vacuum. ZIF-8@MTPN (0.16 g) and methanol (18 mL) were added to a Falcon tube. After acetic acid (2 mL) being added, the mixture was stirred at room temperature for 30 min. The H-MTPN was retrieved by centrifugation, washed with methanol, and dried under vacuum.

Synthetic procedure for H-MTPN-TCNE

H-MTPN (60 mg, internal alkyne 0.28 mmol based on elemental analysis of nitrogen), tetracyanoethylene (86 mg, 0.67 mmol), and 1,2-dichloroethane (18 mL) were added to a flame-dried 50 mL Schlenk flask. The mixture was sonicated for 30 min and heated at 60 °C for 2 days. During this process, the color of powder changed from orange to dark. H-MTPN-TCNE was retrieved by centrifugation, washed with methanol, and dried under vacuum.

Synthetic procedure for model compounds, TP and TP-TCNE

The model compound, TP was prepared by the synthetic procedure in the literature.⁴ In our work, 4iodophenyldiphenylamine (0.58 g, 1.7 mmol), 4-ethynylphenyldiphenylamine (0.54 g, 2.0 mmol), (PPh₃)₂PdCl₂ (0.12 g, 0.17 mmol), CuI (32 mg, 0.17 mmol), triethylamine (10 mL), and THF (20 mL) were added to a flamedried 100 mL Schlenk flask. The reaction mixture was heated at 80 °C overnight. After being cooled to room temperature, the solvent was evaporated. The product was extracted with methylene and water. After the solution being dried by MgSO₄, the solvent was evaporated. The product, TP was separated by column chromatography using an 8:1 mixture of hexane and methylene chloride as an eluent. TP is a known compound⁴ and ¹H and ¹³C NMR spectra matched well with that in the literature. ¹H NMR of TP: (500 MHz, CDCl₃): δ = 7.35 (d, *J* = 8.8 Hz, 4 H), 7.30-7.24 (m, 8 H), 7.13-7.09 (m, 8 H), 7.07-7.03 (m, 4 H), 7.00 (d, *J* = 8.8 Hz, 4 H) ppm. ¹³C NMR of TP: (125MHz, CDCl₃): δ = 147.6, 147.3, 132.4, 129.5, 129.4, 125.3, 124.9, 123.4, 122.5, 116.6, 88.8 ppm.

For the preparation of TP-TCNE, TP (0.26 g, 0.51 mmol), TCNE (65 mg, 0.51 mmol), and 1,2-dichloroethane (15 mL) were added to a flame-dried 50 mL Schlenk flask. The mixture was heated at 60 °C overnight. During this process, the color of the solution changed from pale yellow to dark. After being cooled to room temperature, the solvent was evaporated. The product was extracted using methylene chloride and water. After the solution being dried by MgSO₄, the solvent was evaporated. The product was separated by column chromatography using an 1:1 mixture of hexane and methylene chloride as an eluent. TP-TCNE is an unknown compound and was characterized fully as following. Characterization data of TP-TCNE: isolated yield: 89 %, ¹H NMR (500 MHz, CDCl₃): δ = 7.65 (d, *J* = 9.2 Hz, 4 H), 7.39 (t, *J* = 7.9 Hz, 8 H), 7.29-7.23 (m, 8 H), 7.23-7.18 (m, 8 H), 6.90 (d, *J* = 9.2 Hz, 4 H) ppm. ¹³C NMR (125MHz, CDCl₃): δ = 165.2, 153.6, 144.7, 131.9, 130.1, 126.9, 126.6, 121.9, 118.1, 113.7, 112.8, 78.2 ppm. HRMS (EI⁺) of C₄₄H₂₈N₆: calc. 640.2375, obs. 640.2375. (Refer to the ¹H and ¹³C spectra in Fig. S1.)

Electrochemical performance studies

The electrochemical cells were fabricated by following the procedure in the literature.⁵ In our work, for the preparation of working electrodes, H-MTPN or H-MTPN-TCNE (15 mg), polyvinylidene fluoride binder (10 mg), and Super P carbon black (40 mg) were well mixed in *N*-methylpyrrolidone. Al foil was then coated with this mixture and dried under vacuum at 110 °C for 1 d. The material coated Al electrodes were cut into a circular shape with a 1.4 cm diameter. Electrochemical cells were assembled in a glove box filled with argon. Coin-type half cells (CR2032 type) were used. Li metal was used as the counter electrode. 1 M LiPF₆ in EC/DMC (1:1 v/v) was used as the electrolyte. The discharge/charge cycle tests were conducted using a WBCS3000 automatic battery cycler system. The cells were cycled between 4.2 V and 1.5 V (vs Li/Li⁺).

For the investigation of cycled materials, the cells were disassembled. The working electrode was treated with sonication in methanol. The detached materials were washed with methanol and dried under vacuum. The powder was investigated by SEM. (Refer to Figs. S3-4)

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Fig. S1 Low magnification TEM image of H-MTPN-TCNE.







Fig. S3 Cycle tests of H-MTPN and H-MTPN-TCNE with a 100 mA/g current density.





Fig. S4 Charge-discharge profiles of (a) H-MTPN and (b) H-MTPN-TCNE.

Fig. S5 Charging profiles of H-MTPN-TCNE depending on current density.



Fig. S6 Cyclovoltammograms of TP-TCNE and TP (5 mM in 0.1 M TBAPF₆ in CH_2Cl_2 , reference electrode: Ag/AgNO₃, counter electrode: Pt wire, scan rate 100 mV/s, and scan direction: positive scan first from 0 V, negative scan second, and then positive scan third).





Fig. S7 Cyclovoltammograms of (a) H-MTPN and (b) H-MTPN-TCNE (scan rate: 0.5 mV/s).

Fig. S8 SEM images of H-MTPN-TCNE recovered after cycles.





