# Supporting Information

# High-voltage (4.1 V) organic electrode material with oxygen redox center

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#### **Experimental Procedures**

#### **Preparation of materials**

DD and 4,5-difluorophthalonitrile were purchased from Tokyo Chemical Industry Co., Ltd (Japan) and used without further purification. Potassium carbonate and dichloromethane were purchased from Daejung (Korea). Methanol was purchased from Samchun (Korea). Anhydrous DMF was purchased from Alfa Aesar (USA). 2,3,6,7,13,14-hexahydroxy-9,10dimethyltriptycene was synthesized according to the literature procedure.<sup>1</sup> Unless otherwise noted, all reagents were purchased from commercial suppliers and used as received. All airsensitive manipulations were carried out under  $N_2$ /Ar atmosphere by standard Schlenk-line techniques.

#### **Electrochemical measurements**

Solution samples were prepared and evaluated in an Ar-filled glove box under an inert atmosphere (< 0.5 ppm O<sub>2</sub>, H<sub>2</sub>O). Cyclic voltammograms of 5,10-dihydro-5,10dimethylphenazine (DMPZ), thianthrene (TA), and **DD** (concentration = 10 mM) were obtained using 0.1 M LiClO<sub>4</sub> in EC/DMC (v/v 1:1). A three-electrode system (Pt counter electrode; Ag/AgNO<sub>3</sub> reference electrode; glassy carbon working electrode) was employed, and a scan rate of 100 mV s<sup>-1</sup> was used.

Voltage–capacity profiles of **DD** and **3D-DD** versus Li metal foil (Hohsen, Japan) were obtained in coin-type cells (CR2032). The Li metal anode was prepared in an Ar-filled glove box. The cathodes (6–8 mg) were fabricated by mixing 40% (w/w) active materials, 40% (w/w) carbon black, and 20% (w/w) polytetrafluoroethylene (PTFE, Aldrich) binder. A porous glass microfiber membrane (GF/F; Whatman, UK) was used as a separator in the Li cells. The electrolytes were 5 M LiClO<sub>4</sub> in EC/DMC (1:1, v/v) and 3M LiTFSI in EC/DMC (1:1, v/v); the cells were assembled under inert atmosphere within an Ar-filled glove box. Electrochemical

measurements were performed at a constant current density of 50 mA  $g^{-1}$  in the voltage range of 2–4.3 V or 3–4.4 V versus Li/Li<sup>+</sup> using a battery test system (Won-A Tech, Korea).

#### Ex situ electrode characterization

The electrode materials of **DD** and **3D-DD** at different states of cell cycling (i.e., pristine, fully-charged, and fully-discharged) were prepared by disassembling the coin cells and rinsing the electrodes with EC/DMC. FT-IR spectra were obtained on an FT/IR–4200 (Jasco, Japan) at a resolution of 4 cm<sup>-1</sup>; sample pellets were made of the electrode materials at different states and KBr powder. XPS measurements were performed using an Axis Supra<sup>TM</sup> spectrometer (Kratos, U.K.). All the measured spectra were set to the reference of C 1s (284.4 eV), which is correlated to the Super P.

#### **Physical Measurements.**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 500 MHz Varian/Oxford As-500 spectrometer. Chemical shifts were referenced to the residual solvent peaks.<sup>2</sup> FT-IR spectra for the characterization of **3D-DD** were recorded on a Shimadzu IRTracer–100 FT-IR Spectrophotometer. Elemental analysis was performed by a Perkin Elmer 2400 Series II CHNS/O Analyzer.

#### Triptycene[2,3-b:6,7-b':12,13-b'']tris(1,4-benzodioxin-6,7-dicarbonitrile) (3D-DD).

A mixture of 2,3,6,7,13,14-hexahydroxy-9,10-dimethyltriptycene<sup>1</sup> (0.400 g, 1.06 mmol), 4,5-difluorophthalonitrile (0.696 g, 4.24 mmol), and potassium carbonate (1.326 g, 9.596 mmol) in anhyd DMF (10 mL) was stirred at 80 °C for 13 h under N<sub>2</sub>/Ar atmosphere. After the reaction was complete, the mixture was cooled to r.t., and poured into water (25 mL). The precipitates were isolated by filtration, and washed sequentially with water (25 mL),

MeOH (25 mL), and DCM (25 mL). The remaining solid was dried under a stream of air to afford **3D-DD** as a light tan powder (0.7352 g, 0.9794 mmol, yield = 93%). <sup>1</sup>H NMR (500 MHz, DMSO, 298 K):  $\delta$  7.75 (s, 6H), 6.99 (s, 6H), 2.18 (s, 6H). <sup>13</sup>C NMR (125 MHz, DMSO, 298 K)  $\delta$  145.2, 144.2, 137.0, 121.7, 115.1, 110.8, 110.1, 47.4, 13.1. FT-IR (ATR, cm<sup>-1</sup>): 3059, 2235, 1638, 1614, 1597, 1566, 1503, 1472, 1456, 1381, 1331, 1261, 1179, 1084, 972, 899, 800, 735. Anal. Calcd for C<sub>46</sub>H<sub>20</sub>N<sub>6</sub>O<sub>7</sub> (**3D-DD**·H<sub>2</sub>O): C, 71.88; H, 2.62; N, 10.93. Found: C, 71.73; H, 2.46; N, 11.02.

#### X-ray Crystallographic Studies on 3D-DD.

Single crystals of **3D-DD** were prepared by slow diffusion of Et<sub>2</sub>O into a DMSO solution of this material. A yellow crystal (approximate dimensions  $0.09 \times 0.135 \times 0.256$  mm<sup>3</sup>) was placed onto a nylon loop with Paratone-N oil, and mounted on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The data collection was carried out using CuKa radiation and the crystal was kept at 93 K. A total of 87677 reflections were measured (6.264°  $\leq 2\theta \leq 159.912^{\circ}$ ). The structure was solved with SHELXT<sup>3</sup> using direct methods, and refined with SHELXL<sup>4</sup> refinement package of OLEX2.<sup>5</sup> A total of 22883 unique reflections were used in all calculations. The final R1 was 0.1635 ( $I \geq 2\sigma(I)$ ) and *wR*2 was 0.4841 (all data).

#### Scanning Transmission X-ray microscopy (STXM).

Chemical phase distribution maps were collected by using STXM combined with Xray absorption spectroscopy (XAS) at the elliptically polarizing undulator beamlines (7.0.1.2 and 11.0.2.2) at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA (USA).<sup>6</sup> After disassembling the coin cells and rinsing the electrodes with EC/DMC, the DD powders at different states of charge (i.e., pristine, fully-charged, fullydischarged, half-charged, and half-discharged) were drop-casted onto a 50-nm-thick SiN<sub>x</sub> window to ensure transparency of samples in soft X-ray region. Image spectra across the O *K*-edge attained spectral sensitivity with the finest energy step of 0.25 eV near the white-line features (Figure S5) from each pixel. In order to choose the optimized imaging parameters with consideration of the required spatial/spectral resolutions and radiation stability, the preliminary dose test verified the maximum allowed dose without structural and chemical changes with varying the dwell times/pixel ( $0.1 \sim 10 \text{ msec}$ ), slit sizes, and pixel sizes ( $50 \sim 200 \text{ nm}$ ). Aligned STXM images with sub-pixel precision were converted to the optical density images by following Beer's law and then filtered by local-means to enhance the signal-to-noise ratio. The quantitative chemical compositions of distinct chemical phases at each pixel were analyzed by linear superposition of the reference spectra (Figure 2d and S5).

#### **Computational details.**

**DD.** For geometry optimization, total energy evaluation, and electron density calculation of the molecules, Gaussian09 quantum chemistry package<sup>7</sup> was used. We exploited spin-unrestricted density functional theory (DFT) and Becke–Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional level of theory<sup>8-10</sup> for all molecule, based on triple-zeta valence polarization (TZVP) basis set.<sup>11</sup> To estimate the solvation effect of the electrolyte (EC/DMC,  $\varepsilon = 46$ ), the implicit solvation methodology, i.e., polarizable continuum model (PCM) scheme, was used. Atomic charge densities of the molecules were evaluated by natural population analysis.<sup>12</sup>

**3D-DD and DD(CN)**<sub>2</sub>. Ground-state geometry optimization, molecular orbital computation, and molecular electrostatic potential map generation were all carried out by using B3LYP-D3BJ<sup>13</sup> density functional with TZVP basis set to properly address the effects of dispersion interaction on hyperconjugation. The entire calculations were performed with Gaussian '09 Revision E.01 software.<sup>7</sup>

## Supplementary figures



**Figure S1.** Frontier molecular orbital (FMO) energies of **DD**, **DD**<sup>+</sup>, EC, and DMC. The energy levels of **DD** change upon oxidation due to the relaxation effect.



Figure S2. (a) Voltage-capacity curve of DD for 1, 2, and 5 cycles. (b) Differential capacity (dQ/dV) curve of DD.



**Figure S3. Capacity-voltage profile of DD in 5 M LiClO**<sub>4</sub> **in TEGDME electrolyte.** The organic redox-active compounds exhibit a higher redox potential in TEGDME-based electrolytes than that obtained in EC/DMC-based electrolytes since the redox potential of organic redox-active species increases with the donor numbers of the electrolytes employed.<sup>14, 15</sup> Accordingly, it showed poor reversibility, exhibiting rapid capacity fading and loss of redox activity within a few cycles due to the electrolyte decomposition at the extremely high operation voltage range. As a result, in the case of p-type organic electrodes, selecting the optimal electrolyte is highly emphasized to exhibit a stable and reversible redox behavior.



Figure S4. Rate capability of DD at current rates of 150, 300, 500, 1000, and 1500 mA  $g^{-1}$ .



Figure S5. ex-situ XPS Cl 2p spectra of DD at noted state-of-charges.



**Figure S6**. Charge distribution calculations of **DD** and **DD**<sup>+</sup> using natural population analysis (NPA).



**Figure S7**. Ex-situ soft X-ray absorption spectroscopy (sXAS) O K-edge spectra of the rest, fully charged, and fully discharged **DD**. The observed **DD** particles are suspected of slight beam damage, exhibiting the imperfect reversibility.



**Figure S8**. Scanning electron microscopy (SEM) images (**a**) with 5k and (**b**) 30k magnification of **DD** electrodes. White arrows indicate the **DD** particles in the electrode.



Figure S9. Cycle stability curve of DD.



**Figure S10**. Solubility test of **DD** (left) and **3D-DD** (right). Photographic image shows a clear solution sample of **DD** (92.1 mg, 500 µmol) in EC/DMC (2 mL) (left) *vs*. a thick suspension of **3D-DD** (2.34 mg, 1.56 µmol) in the same amount of solvent mixture (right).



Figure S11. (a) Design concept and synthesis of **3D-DD**. (b) ORTEP diagram of **3D-DD** with thermal ellipsoids at the 50% probability level.



Figure S12. Ex-situ XRD analysis of **3D-DD**. (SOC [%] is the state-of-charge, indicating the amount of charge left in a battery.)



Figure S13. CV curves for 1 mM 3D-DD in 0.1 M LiTFSI in EC/DMC for three cycles.



Figure S14. Charge/discharge curves of DD(CN)<sub>2</sub>.



Figure S15. <sup>1</sup>H NMR (500 MHz) spectrum of **3D-DD** in CDCl<sub>3</sub> (T = 298 K).



Figure S16. <sup>13</sup>C NMR (125 MHz) spectrum of **3D-DD** in CDCl<sub>3</sub> (T = 298 K).

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