Supplementary Information

High-capacity organic cathode active materials of 2,2′-bis-p-benzoquinone derivatives for rechargeable batteries

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Contents

Fig. S1–S12 and Table S1 S2
Electrolyte effects in charge-discharge curves and cycle performance S8
Experimental details of preparations for cathode active materials S9
Experimental details of DFT calculation and Gaussian archives S15
Solubility study of BBQ derivatives S20
References S21
1H and 13C NMR of compounds involved in this study S22
**Fig. S1** Charge-discharge curves and cycle-life performance over eight cycles for (a) BQ and (b) NDQ cells in 1.0 M LiPF$_6$-EC/DEC.

**Fig. S2** CV of NDQ in acetonitrile.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{1/2}$ in solution CV (V)</th>
<th>Discharge voltage (V)</th>
<th>LUMO level (eV)</th>
<th>HOMO level (eV)</th>
</tr>
</thead>
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<tr>
<td>BQ</td>
<td>-0.91</td>
<td>2.8</td>
<td>-3.947</td>
<td>-7.797</td>
</tr>
<tr>
<td>BBQ</td>
<td>-0.76</td>
<td>2.9</td>
<td>-4.251</td>
<td>-7.736</td>
</tr>
<tr>
<td>NDQ</td>
<td>-0.34</td>
<td>1.8-3.4</td>
<td>-4.645</td>
<td>-7.404</td>
</tr>
</tbody>
</table>

DFT calculations were carried out on the B3LYP/6-31+G* level.
**Fig. S3**  Electrode CVs of (a) Br$_2$- and (b) Me$_2$-BBQ cells (1.0 M LiPF$_6$-EC/DEC) at initial cycle.

**Fig. S4**  Electrode CVs of BBQ cells (1.0 M LiPF$_6$-EC/DEC) from first to eighth cycles.

**Fig. S5**  Cycle-life performance over twenty cycles for cells based on R$_2$-BBQ (R = Br, Me, nBu, and iPr) in 2.75 M LiTFSI-tetraglyme systems.
Fig. S6 Charge-discharge curves and cycle-life performance over eight cycles for (a) F₂⁻, (b) Cl₂⁻, (c) Br₂⁻, (d) Me₂⁻, (e) nBu₂⁻, (f) iPr₂⁻, (g) tBu₂⁻, and (h) (OMe)_2-BBQ cells in 2.75 M LiTFSI-tetraglyme systems.
Fig. S7  CV of (a) F$_2^-$, (b) Cl$_2^-$, (c) Br$_2^-$, (d) Me$_2^-$, (e) nBu$_2^-$, (f) iPr$_2^-$, (g) tBu$_2^-$, and (h) (OMe)$_2$-BBQ in acetonitrile.
Fig. S8  Electrode CV of (OMe)$_2$-BBQ cells at initial cycle.

Fig. S9  Cycle-life performance over twenty cycles for cells based on (a) Cl-BQ and Cl$_2$-BBQ, and (b) OMe-BQ and (OMe)$_2$-BBQ in 2.75 M LiTFSI-tetraglyme systems.
**Fig. S10**  Charge-discharge curves and cycle-life performance over eight cycles for (a) Cl-BQ, (b) Me-BQ, and (c) OMe-BQ in 2.75 M LiTFSI-tetraglyme systems.

**Fig. S11**  Cycle-life performance over 50th cycles for cells based on (OMe)$_2$-BBQ in 2.75 M LiTFSI-tetraglyme systems.

**Fig. S12**  Cyclability for Br$_2$-BBQ cells in 1.0 M LiPF$_6$-EC/DEC, 1.0 M LiTFSI-EiPS, and 2.75 M LiTFSI-tetraglyme systems.
Electrolyte effects in charge-discharge curves and cycle performance

Effects of the electrolyte in the BBQ cell was examined by preparing cells with three different electrolytes: EiPS with 1.0 M Li[N(SO$_2$CF$_3$)$_2$] (LiTFSI), tetraglyme with 2.75 M LiTFSI, and a mixture of EC (30 vol%) and DEC (70 vol%) with 1.0 M LiPF$_6$. The cyclability for the BBQ cells in different electrolytes is shown in Fig. S12, and the charge-discharge curves over eight cycles are depicted in Fig. S13. The LiTFSI-EiPS system provided the highest initial capacity of 429 Ah kg$^{-1}$, which exceeded the theoretical value involving three electrons (376 Ah kg$^{-1}$). However, its discharge capacity significantly faded to 370 Ah kg$^{-1}$ in the second cycle. In the LiTFSI-tetraglyme system, the cell afforded an initial capacity of 358 Ah kg$^{-1}$, and surprisingly increased to 368 Ah kg$^{-1}$ in the second cycle. Although the initial capacity in the tetraglyme system was smaller than in the EiPS system, tetraglyme afforded the highest cycle retention rate (the ratios of the 20th capacity to the 1st in the tetraglyme, EiPS, and EC/DEC systems were 67, 47, and 52%, respectively), and its capacity remained at 239 Ah kg$^{-1}$ at the 20th cycle.

![Fig. S13](image1)

**Fig. S13** Cyclability over twenty cycles for BBQ cells in 1.0 M LiPF$_6$-EC/DEC, 1.0 M LiTFSI-EiPS, and 2.75 M LiTFSI-tetraglyme systems: plots of (a) capacity retention rate versus cycle number and (b) capacity retention rate versus cycle number.

![Fig. S14](image2)

**Fig. S14** Charge-discharge curves and cycle-life performance over eight cycles for BBQ cells in (a) 1.0 M LiTFSI-EiPS, and (b) 2.75 M LiTFSI-tetraglyme systems.
Experimental details of preparations for cathode active materials

Melting points were obtained with a Yanako micro melting point apparatus and are not corrected. Products were purified by flash chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N (spherical, neutral), 63-210 μm). ¹H NMR spectra were recorded with JEOL-ECP-500 (500 MHz) and JEOL-ECP-400 (400 MHz) spectrometers in CDCl₃ or DMSO-d₆. Chemical shifts were reported in parts per million (δ) referenced to the solvent peak at 7.26 or 2.49 ppm. ¹³C NMR spectra were recorded with JEOL-ECP-500 (126 MHz) and JEOL-ECP-400 (100 MHz) spectrometers in CDCl₃ or DMSO-d₆, and referenced to the solvent peak at 77.0 or 39.7 ppm. Coupling constants, J, were reported in Hertz (Hz), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), sext (sextet), sept (septet), dd (double doublet), dt (double triplet) and m (multiplet). IR spectra were obtained on a JASCO FT/IR-4100 or a JASCO FT/IR-5300 spectrometer; absorptions were reported in reciprocal centimeters. Conventional mass spectra were recorded with SHIMADZU GCMS-QP2010Plus and JEOL MS-700 spectrometers, and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1,4,5,8-Naphthodiquinone (NDQ)
A mixture of 1 (570 mg, 3.00 mmol) and [bis(trifluoroacetoxy)iodo]benzene (3.02 g, 7.02 mmol) in acetone (20 mL) was stirred for 1.5 h at room temperature. Then, [bis(trifluoroacetoxy)iodo]benzene (3.44 g, 8.00 mmol) was added to the reaction mixture, and the mixture was stirred at room temperature. After stirring for 2.5 h, the mixture was filtered through a glass filter, and the residue was washed with acetone and benzene, and then dried over under reduced pressure to yield NDQ (86 mg, 15%) as a brown solid. M.p. 204.5–208.0 °C; IR (KBr): ν = 3065, 1685, 1642, 1606, 1299, 1132, 865 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ = 6.89 (s, 4H; vinyl-H); ¹³C NMR (126 MHz, DMSO-d₆): δ = 186.0, 136.1, 126.3 ppm.

2,2'-Bis-p-benzoquinone (BBQ)
A mixture of 2 (2.75 g, 19.9 mmol), iodine (2.03 g, 8.01 mmol), acetic acid (1.04 g, 5.92 mmol), acetic acid (33 mL), water (7 mL), and sulfuric acid (1 mL) was heated to 60 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into 10% aqueous NaHSO₃. The insoluble precipitate was filtered off using a glass filter, and then washed with diethyl ether. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 2/1) to yield 3 (3.90 g, 74%) as a colorless liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.33 (d, J = 2.8 Hz, 1H; CICH₂), 6.85 (dd, J = 9.2, 3.2 Hz, 1H; CIC(OC₃H₇)CHCH₂), 6.74 (d, J = 8.7 Hz, 1H; CIC(OC₃H₇)CH₂), 3.81 (s, 3H; OCH₃), 3.74 (s,
3H; OCH₃) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 154.1, 152.5, 124.7, 114.6, 111.5, 85.9, 56.9, 55.8 ppm; LRMS (EI): m/z (%): 264 (100) [M⁺], 249 (78), 122 (18), 107 (23), 79 (22).

A mixture of 3 (5.84 g, 22.1 mmol), copper (7.76 g, 122 mmol), 2,2'-bipyridine (347 mg, 2.22 mmol), and DMSO (40 mL) was heated at 150 °C under N₂ for 15 h. After cooling to room temperature, water (80 mL) was added with cooling by an ice bath. The mixture was then filtered through a pad of Celite and the pad was washed with diethyl ether. The aqueous layer was separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: hexane–chloroform = 1/1 and 100% chloroform) to yield 4 (1.99 g, 66%) as a white crystalline solid. M.p. 96.0–98.0 °C; ¹H NMR (500 MHz, CDCl₃): δ = 6.91 (d, J = 8.7 Hz, 2H; CC(OCH₃)CH), 6.86 (dd, J = 8.7, 3.2 Hz, 2H; CC(OCH₃)CHCH), 6.84 (d, J = 3.3 Hz, 2H; CCH(OCH₃),) 3.78 (s, 6H; OCH₃), 3.73 (s, 6H; OCH₃) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 153.2, 151.2, 128.5, 117.1, 113.3, 112.4, 56.4, 55.6 ppm; LRMS (EI): m/z (%): 274 (100) [M⁺], 259 (42), 244 (26), 228 (37), 213 (17).

To a mixture of 4 (551 mg, 2.01 mmol) in acetonitrile (15 mL), a solution of CAN (11.0 g, 6.00 mmol) in water (15 mL) was added at 0°C, the mixture was then warmed slowly to room temperature. After stirring for 1 h, water (60 mL) and dichloromethane (30 mL) was added to the mixture. The aqueous layer was then separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: 100% chloroform and chloroform–ethyl acetate = 20/1) to yield BBQ (294 mg, 68%) as a yellow crystalline solid. M.p. 184.5–191.0 °C; IR (KBr): ν = 1657, 1594, 1351, 1293, 1280, 1101, 928, 918, 847 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 6.89 (d, J = 10.1 Hz, 2H; COCH₃), 6.86 (dd, J = 10.1, 2.3 Hz, 2H; COOCH₃), 6.83 (d, J = 2.3 Hz, 2H; CCH.CO) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 186.2, 184.4, 139.9, 136.8, 136.6, 135.8 ppm; LRMS (EI): m/z (%): 214 (63) [M⁺], 186 (23), 130 (28), 102 (36), 82 (58), 54 (69), 50 (27), 44 (100).

5,5'-Difluoro-2,2'-bis-p-benzoquinone (F₂-BBQ)

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of 5 (625 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield F₂-BBQ (195 mg, 39%) as a yellow solid. M.p. 183.0–185.0 °C; IR (KBr): ν = 1685, 1656, 1604, 1357, 1163, 921 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.87 (d, J = 7.6 Hz, 2H; CCH.CO), 6.57 (d, J = 10.0 Hz, 2H; CFCH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 184.1 (d, J = 14.3 Hz), 178.3 (d, J = 24.8 Hz), 159.6 (d, J = 292.2 Hz), 139.4, 134.4 (d, J = 2.8 Hz), 115.7 (d, J = 9.5 Hz) ppm; LRMS (EI): m/z (%): 250 (100) [M⁺], 129 (58), 73 (77), 69 (64), 60 (53), 57 (61), 55 (62); HRMS (EI): found [M⁺] 250.0073, C₁₀H₆F₂O₄⁺ requires 250.0078.

S10
**5,5'-Dichloro-2,2'-bis-p-benzoquinone (Cl₂-BBQ)**

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of 6 (690 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water, and dried over under reduced pressure. Then, the residue was purified by column chromatography on silica gel (eluent: 100% chloroform), and by washing with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield Cl₂-BBQ (176 mg, 31%) as a yellow solid. M.p. 196.0–199.0 °C; IR (KBr): ν = 1670, 1653, 1608, 1570, 1320, 1194, 1010, 910 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.12 (s, 2H; CCIC₃H), 7.00 (s, 2H; CCHCO) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ = 182.8, 179.0, 143.1, 139.6, 136.0, 134.2 ppm; LRMS (EI): m/z (%): 286 (25), 284 (44), 282 (56) [M⁺], 149 (75), 84 (44), 81 (50), 73 (37), 69 (100), 57 (48), 55 (40).

**5,5'-Dibromo-2,2'-bis-p-benzoquinone (Br₂-BBQ)**

To a mixture of CAN (7.24 g, 13.2 mmol) in water (12 mL), a solution of 7 (868 mg, 4.00 mmol) in acetonitrile (12 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (60 mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and chloroform / hexane = 1 : 1, then dried over under reduced pressure to yield Br₂-BBQ (187 mg, 25%) as a yellow solid. M.p. 188.5–191.0 °C; IR (KBr): ν = 1664, 1604, 1571, 1318, 1189, 984, 910, 438 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (s, 2H; CBrCH₃), 7.04 (s, 2H; CCHCO) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 181.7, 178.4, 139.0, 138.2, 137.7, 135.6 ppm; LRMS (EI): m/z (%): 374 (57), 372 (85), 370 (41) [M⁺], 149 (40), 86 (44), 84 (63), 81 (49), 73 (41), 69 (100), 57 (45), 55 (43).

**5,5'-Dimethyl-2,2'-bis-p-benzoquinone (Me₂-BBQ)**

To a mixture of CAN (3.61 g, 6.60 mmol) in water (6 mL), a solution of 8 (304 mg, 2.00 mmol) in acetonitrile (6 mL) was added dropwise at room temperature. After stirring for 1 h, water (40 mL) was added to the mixture, and the mixture was filtered through a glass filter. The crude product obtained was washed with water, and then dried over under reduced pressure. The residue was recrystallized from chloroform / ethanol to yield Me₂-BBQ (164 mg, 68%) as a yellow solid. Decomposition 167.0 °C; IR (KBr): ν = 1649, 1629, 1577, 1234, 1205 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.81 (s, 2H; CCHCO), 6.70 (d, J = 1.6 Hz, 2H; C(CH₃)CH₂), 2.10 (d, J = 1.2 Hz, 6H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 186.9, 184.7, 146.2, 139.5, 135.9, 133.6, 15.6 ppm; LRMS (EI): m/z (%): 242 (100) [M⁺], 146 (82), 118 (24), 68 (41), 40 (37).

**5,5'-Dimethoxy-2,2'-bis-p-benzoquinone ((OMe)₂-BBQ)**

To a mixture of CAN (18.1 g, 33.0 mmol) in water (30 mL), a solution of 9 (1.68 g, 10.0 mmol) in acetonitrile (30 mL) was added dropwise at room temperature. After stirring for 1.5 h, water (150
mL) was added to the mixture, and the mixture was filtered through a glass filter. The residue was washed with water and methanol, then dried over under reduced pressure to yield (OMe)2-BBQ (93 mg, 7%) as a yellow solid. Decomposition 214.0 °C; IR (KBr): ν = 1671, 1643, 1620, 1574, 1225, 1197, 1173, 998, 910 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.77 (s, 2H; C(OCH₃)CH), 6.04 (s, 2H; CCHCO), 3.87 (s, 6H; OCH₃) ppm; Measurement of ¹³C NMR was unsuccessful because of low solubility of the product in general organic solvents; LRMS (EI): m/z (%): 274 (100) [M⁺], 245 (47), 231 (37), 201 (21), 69 (24).

5,5'-Dibutyl-2,2'-bis-p-benzoquinone (nBu₂-BBQ)
To a mixture of 2 (277 mg, 2.00 mmol) and TMEDA (621 mg, 5.40 mmol) in dry hexane (4 mL), n-butyllithium (1.6 M hexane solution, 2.91 g, 6.00 mmol) was added dropwise at room temperature under N₂. After stirring for 20 h, the reaction mixture was cooled by an ice bath, 1-bromobutane (1.154 g, 8.40 mmol) was then added dropwise to the mixture, and the mixture was warmed slowly to room temperature. After stirring for 12 h, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was separated and extracted with diethyl ether. The combined organic layer was then washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 4/1) to yield 10 (84 mg, 22%) as a colorless liquid. IR (neat): ν = 2954, 2931, 1501, 1465, 1224, 1050 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.76 (d, J = 8.4 Hz, 1H; CC(OCH₃)CH), 6.73 (d, J = 3.2 Hz, 1H; C(CH₃)(OCH₃)), 6.68 (dd, J = 8.8, 3.2 Hz, 1H; CC(OCH₃)CHCH), 3.78 (s, 3H; OCH₃), 3.76 (s, 3H; OCH₃), 2.58 (t, J = 7.2 Hz, 2H; Ar-CH₂), 1.59-1.52 (m, 2H; ArCH₂CH₂), 1.37 (sext, J = 7.2 Hz, 2H; CH₂CH₂), 0.93 (t, J = 7.6 Hz, 3H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 153.3, 151.7, 132.4, 116.1, 110.9, 110.3, 55.6, 55.3, 32.0, 29.9, 22.5, 13.9 ppm; LRMS (EI): m/z (%): 194 (90) [M⁺], 152 (30), 151 (100), 137 (68), 121 (51), 91 (27), 77 (19).

To a mixture of CAN (3.77 g, 6.87 mmol) in water (15 mL), a solution of 10 (403 mg, 2.10 mmol) in acetonitrile (6 mL) was added dropwise at room temperature. After stirring for 1 h, water (60 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield nBu₂-BBQ (220 mg, 65%) as a yellow crystalline solid. M.p. 167.5–169.0 °C; IR (KBr): ν = 2953, 2926, 1661, 1646, 923 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.80 (s, 2H; CCHCO), 6.65 (t, J = 1.6 Hz, 2H; C(nBu)CH), 2.46 (dt, J = 7.8, 1.2 Hz, 4H; CCH₂), 1.55-1.48 (m, 4H; CCH₂CH₂), 1.41 (sext, J = 7.2 Hz, 4H; CH₂CH₂), 0.95 (t, J = 7.2 Hz, 6H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 186.8, 185.0, 150.0, 139.2, 136.2, 132.6, 29.8, 28.5, 22.4, 13.8 ppm; LRMS (EI): m/z (%): 328 (11), 327 (11) [M+H⁺], 155 (22), 138 (28), 137 (69), 136 (100), 107 (33), 91 (24), 90 (26), 89 (34), 77 (32).

5,5'-Diisopropyl-2,2'-bis-p-benzoquinone (iPr₂-BBQ)
To a mixture of n-butyllithium (1.6 M hexane solution, 2.1 mL, 3.3 mmol) in dry THF (1 mL), a
solution of 2 (279 mg, 2.00 mmol) in dry THF (1.6 mL) was added at room temperature under argon. After stirring for 1 h, acetone (480 mg, 8.20 mmol) dissolved in dry THF (2.2 mL) was slowly added. After stirring for 1 h, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–ether = 1/2) to yield 11 (186 mg, 47%) as a yellow liquid. IR (neat): ν = 3444, 2965, 2939, 2834, 1491, 1464, 1420, 1281, 1218, 1178, 1070, 1050, 1026 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.91 (d, J = 3.2 Hz, 1H; CC(OCH₃)H), 6.85 (d, J = 8.6 Hz, 1H; CC(OCH₃)CH), 6.74 (dd, J = 8.8, 3.2 Hz, 1H; CC(OCH₃)CHCH), 4.25 (s, 1H; OH), 3.88 (s, 3H; OCH₃), 3.78 (s, 3H; OCH₃), 1.59 (s, 6H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 153.5, 151.0, 137.1, 113.0, 111.9, 111.1, 72.4, 55.7, 55.6, 29.5 ppm; LRMS (EI): m/z (%): 196 (47) [M⁺], 181 (98), 43 (100).

To a mixture of 10% palladium on carbon (43 mg) and 11 (372 mg, 1.90 mmol) in ethyl acetate (5 mL), a drop of sulfuric acid was added, then the mixture was stirred at room temperature under the atmosphere of hydrogen using a balloon. After stirring for 24 h, water (50 mL) was added dropwise to the mixture. The palladium on carbon was filtered off, and the aqueous layer was separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–chloroform = 4/1) to yield 12 (284 mg, 79%) as a yellow liquid. IR (neat): ν = 2959, 1501, 1464, 1281, 1220, 1048 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.84 (d, J = 2.4 Hz, 1H; CC(OCH₃)H), 6.80 (d, J = 8.4 Hz, 1H; CC(OCH₃)CH), 6.70 (dd, J = 8.4, 2.4 Hz, 1H; CC(OCH₃)CHCH), 3.81 (s, 3H; OCH₃), 3.80 (s, 3H; OCH₃), 3.33 (sept, J = 6.8 Hz, 1H; CH), 1.23 (d, J = 7.6 Hz, 6H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 153.7, 151.0, 138.4, 113.0, 111.2, 109.9, 56.0, 55.5, 26.8, 22.7 ppm; LRMS (EI): m/z (%): 180 (74) [M⁺], 165 (100), 150 (50), 105 (17).

To a mixture of CAN (1.15 g, 2.10 mmol) in water (4 mL), a solution of 12 (115 mg, 0.63 mmol) in acetonitrile (4 mL) was added dropwise at room temperature. After stirring for 1 h, water (40 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield iPr₂-BBQ (76 mg, 81%) as a yellow crystalline solid. M.p. 173.5–175.0 °C; IR (KBr): ν = 2966, 1653, 1600, 1233, 1048, 925 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.81 (s, 2H; CCCHO), 6.63 (s, 2H; C(iPr)CH), 3.07 (sept, J = 6.4 Hz, 2H; CH), 1.16 (d, J = 6.8 Hz, 12H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 186.4, 185.4, 155.3, 139.0, 136.4, 130.7, 26.8, 21.3 ppm; LRMS (EI): m/z (%): 300 (19), 299 (15), 298 (8) [M⁺], 154 (27), 149 (100), 136 (26), 83 (27), 81 (28), 71 (44), 69 (43), 57 (35), 55 (27); HRMS (EI): found [M⁺] 298.1193, C₁₈H₁₆O₄ requires 298.1205.

5,5’-Di-tert-butyl-2,2’-bis-p-benzoquinone (tBu₂-BBQ)
To a mixture of sodium hydride (178 mg, 4.40 mmol) in DMF (3 mL), a solution of 13 (334 mg, 2.00
mmol) in DMF (3 mL) was added at room temperature under N₂. Then, methyl iodide (1.36 g, 9.60 mmol) was slowly added to the mixture, and stirred for 4 h at 40 °C. After cooling to room temperature, the mixture was quenched by adding excess amount of water dropwise. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane–ether = 95/5) to yield 14 (323 mg, 83%) as a yellow liquid. IR (neat): ν = 2952, 2927, 1499, 1488, 1464, 1283, 1221, 1059, 1032 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.89 (d, J = 3.2 Hz, 1H; C(tBu)CH), 6.88 (d, J = 8.8 Hz, 1H; C(tBu)C(OCH₃)CH), 6.79 (dd, J = 8.4, 3.2 Hz, 1H; CC(OCH₃)CHCH), 3.80 (s, 3H; OCH₃), 3.77 (s, 3H; OCH₃), 1.36 (s, 9H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 153.2, 152.8, 139.8, 114.2, 112.2, 109.7, 55.6, 55.5, 34.9, 29.6 ppm; LRMS (EI): m/z (%): 194 (56) [M⁺], 179 (100), 164 (36), 151 (36).

To a mixture of CAN (2.71 g, 4.90 mmol) in water (10 mL), a solution of 14 (320 mg, 1.70 mmol) in acetonitrile (10 mL) was added dropwise at room temperature. After stirring for 1 h, water (60 mL) was added to the mixture. The mixture was filtered through a glass filter, and the residue was washed with water and then dried over under reduced pressure. The crude product obtained was recrystallized from chloroform / ethanol to yield /Bu₂-BBQ (150 mg, 56%) as a yellow crystalline solid. M.p. 194.0–196.0 °C; IR (KBr): ν = 2956, 2924, 1658, 1630, 1594, 1362, 1237, 914 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 6.75 (s, 2H; CCHCO), 6.68 (s, 2H; C(tBu)CH), 1.31 (s, 18H; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 186.6, 185.6, 156.4, 138.0, 137.6, 131.9, 35.3, 29.0 ppm; LRMS (EI): m/z (%): 326 (48) [M⁺], 311 (56), 285 (36), 284 (87), 283 (34), 269 (100), 201 (48), 41 (40).
Details of DFT calculations and Gaussian archives of optimized structures at the B3LYP/6-31+G* level

DFT calculations were carried out using GAUSSIAN 09 program.\(^1\) Geometry optimization were performed using standard gradient techniques at the B3LYP level of theory using restricted (RB3LYP) and unrestricted (UB3LYP) methods for closed- and open-shell systems, respectively.\(^2\) In every case, 6-31+G* was used as the basis set, and all ground states were verified by vibration frequency analysis. The calculated molecular structures were visualized by Gauss View 5.0.\(^3\)

The singlet and triplet states of the BBQ dianion, the doublet and quartet states of the trianion, and singlet, triplet, and quintet states of the tetraanion were calculated and summarised in the following Table. BQ dianion and trianion are more stable in singlet and doublet states than in triplet and quartet states, respectively, while BBQ dianion and trianion are more stable in triplet and doublet states than in singlet and quartet states, respectively. Although the BBQ tetraanion had similar energies in singlet and triplet states, the singlet was determined as the most stable state considering that the triplet state was highly spin contaminated.

<table>
<thead>
<tr>
<th>Species</th>
<th>Spin state</th>
<th>Energy (kJ mol(^{-1}))</th>
<th>&lt;S(^2)&gt; value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>BQ dianion</td>
<td>singlet</td>
<td>-1001446.2</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>triplet</td>
<td>-1001326.5</td>
<td>2.082</td>
</tr>
<tr>
<td>BQ trianion</td>
<td>doublet</td>
<td>-1000698.6</td>
<td>0.751</td>
</tr>
<tr>
<td></td>
<td>quartet</td>
<td>-1000623.0</td>
<td>3.822</td>
</tr>
<tr>
<td>BBQ dianion</td>
<td>singlet</td>
<td>-2000099.7</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>triplet</td>
<td>-2000134.6</td>
<td>2.278</td>
</tr>
<tr>
<td>BBQ trianion</td>
<td>doublet</td>
<td>-1999622.3</td>
<td>1.360</td>
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<tr>
<td></td>
<td>quartet</td>
<td>-1999553.6</td>
<td>4.089</td>
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<tr>
<td>BBQ tetraanion</td>
<td>singlet</td>
<td>-1998790.5</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>triplet</td>
<td>-1998789.7</td>
<td>2.598</td>
</tr>
<tr>
<td></td>
<td>quintet</td>
<td>-1998752.0</td>
<td>6.406</td>
</tr>
</tbody>
</table>

* Determined by the HF/6-31+G* level.

BQ

\[^1\]GINC-HEX\(\text{FOpt}\)\(\text{RB3LYP/6-31+G(d)}\)\(\text{YOKOJI}\)\(10-\text{Aug}-2015/0\)\#B3LYP/6-31+G* opt=(ReadFC,Maxcycle=100)\ NoSymm freq=NoRaman geom=check guess=\text{read}\(\text{bqb3+V0.1JC.1.1473960993.0.6385839984.0.000000008C.1.2455936404.1.2457168671.0.0000000035C.0.512664242.1.1884288198.-0.0000000034C.-1.6176902387.-0.1937182215.-0.000000006C.0.7752942945.-0.8008521598.0.0.0423659446.1.6332890664.-0.0000000026H.-2.0720010581.1.9520647157.0.0000000074H.-8.119264774.-2.2335912849.-0.0000000048H.0.341651651.2.6784450456.-0.0000000088O.2.3221669073.0.9923242349.0.000000025O.-2.7924601291.-0.5474613541.0.1H.1.6017108891.-1.5071845781.0.0000000059\ \text{Version=EM64L-G09Rev}=\text{C.01HF}=\text{381.4704834}\ \text{RMSD}=\text{3.710}\ \text{RMSF}=\text{3.710}\ \text{Dipole}=\text{0.0000008,0.0000037,0.3}\ \text{Quadrupole}=\text{-9.3959157,6.9692472,4.266688,5.4190299,0.0.0PG=C01 [X(C6H4O2)]} \}@
BQ anion radical

\[ \text{GINC=HEX} \text{FOPt U3LYPd-6-31+G(d|C6H4O2(2-1)} \]

BQ anion (singlet)

\[ \text{GINC=HEX} \text{FOPt U3LYPd-6-31+G(d|C6H4O2(2-3)} \]

BQ anion (triplet)

\[ \text{BQ radical anion (doublet)} \]

\[ \text{BQ anion (quartet)} \]
[...]

**BBQ**

\[ V\text{G}INC-HEXFO\text{Op}\#B3LYP6-31+G^* \text{ opt=(ReadFC,Maxycle=100) No Symm freq=No Raman geom=check guess=read} \]

\[ \text{BBQ anion radical} \]

\[ V\text{G}INC-HEXFO\text{Op}\#B3LYP6-31+G^* \text{ (C12H6O4-YOKOJI12-Jun-2014@#B3LYP6-31+G* opt=(ReadFC,Maxycle=100) No Symm freq=No Raman geom=check guess=read) \]

**BBQ dianion (singlet)**

\[ V\text{G}INC-HEXFO\text{Op}\#B3LYP6-31+G^* \text{ (C12H6O4-(2-)YOKOJI12-Jun-2014@#B3LYP6-31+G* opt=(CalcFC,Maxycle=100) No Symm freq=No Raman geom=check guess=read) \]

[...]
BBQ dianon (triplet)

\[ \text{BBQ dianon (triplet)} \]

\[ \text{BBQ radical triadion (doublet)} \]

\[ \text{BBQ radical triadion (quartet)} \]
Solubility study of BBQ derivatives

The solubilities of BBQ derivatives were measured for the non-substituted BBQ and R₂-BBQ (R = F, Cl, Br, Me, nBu, and OMe) using tetraglyme as the electrolyte solution. The obtained solubilities and the related battery performance are summarized in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solubility in tetraglyme (g L⁻¹)</th>
<th>Capacity retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBQ</td>
<td>4.0-5.0</td>
<td>67</td>
</tr>
<tr>
<td>F₂-BBQ</td>
<td>18-19</td>
<td>12</td>
</tr>
<tr>
<td>Cl₂-BBQ</td>
<td>9.0-10</td>
<td>68</td>
</tr>
<tr>
<td>Br₂-BBQ</td>
<td>3.0-4.0</td>
<td>&gt;99&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Me₂-BBQ</td>
<td>7.0-8.0</td>
<td>46</td>
</tr>
<tr>
<td>nBu₂-BBQ</td>
<td>&gt;23</td>
<td>37</td>
</tr>
<tr>
<td>(OMe)₂-BBQ</td>
<td>&lt;1.0</td>
<td>60</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio of the 20th capacity to the 1st value. <sup>b</sup>The capacity was rapidly decreased at around 25th cycle.

Experimental method for solubility measurement

R₂-BBQ (0.5 mg) was added to tetraglyme (0.5 mL), and the mixture was stirred at 20 °C for 5 min. The addition of 0.5 mg R₂-BBQ and stirring of the mixture were repeated, until undissolved R₂-BBQ remained after the stirring.
References


$^1$H and $^{13}$C NMR of compounds involved in this study