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Anthraquinone-based Oligomer as a Long Cycle-life Organic Electrode Material for Use in Rechargeable Batteries

Masaru Yao,*^[a] Hikaru Sano,^[a] Hisanori Ando,^[a] Tetsu Kiyobayashi,^[a] and Nobuhiko Takeichi^[a]

Abstract: An anthraquinone (AQ)-based dimer and trimer linked by a triple bond (-C=C-) were newly synthesized as active materials for the positive electrode of rechargeable lithium batteries. These synthesized oligomers exhibited an initial discharge capacity of about 200 mAh g⁻¹ with an average voltage of 2.2-2.3 V vs Li_(C.E.). These capacity values are similar to that of the AQ-monomer, reflecting the two-electron transfer redox per AQ unit. Regarding their cycling stability, the capacity of the monomer electrode quickly decreased; however, the electrodes of the prepared oligomers showed an improved cycling performance. In particular, the discharge capacities of the trimer were almost constant during 100 cycles. A theoretical calculation revealed that the intermolecular binding energy can be increased to the level of a weak covalent bonding by oligomerization, which would be beneficial to suppress the dissolution of the organic active materials into the electrolyte solutions. These results show that the cycle-life of organic active materials can be extended without lowering the discharge capacity by the oligomerization of the redox active molecule unit.

electrolyte solutions^[23] containing additives have been recently reported to have a positive effect for this issue; however, the development of a long cycle-life active material itself based on a new molecular design would be important at the same time. To realize it, we paid attention to the oligomerization technique. As a linker, which connects the AQ unit, a triple bond based on the acetylene structure ($-C \equiv C-$) was chosen. The triple bond is frequently studied as a conductive unit for molecular wires since it has *sp*-hybridization orbitals and shows a conductivity along the bonding direction ^[24,25]. This feature can help the intramolecular electron conduction during the charge/discharge process. In this study, a novel AQ-dimer and trimer connected by the triple bond were synthesized as positive electrode active materials (Figures 1b and 1c), and their charge/discharge behaviors were compared to that of the AQ-monomer.

(b)

1. Introduction

Using redox active organic materials, which do not include any minor metal resources, as positive electrode materials in substitution for the currently used minor metal oxides can be a solution for the resource problem of the present rechargeable lithium batteries. So far, many types of organic active materials have been studied [1-5], and low molecular weight organic derivatives have attracted attention in past years [6-17], since they often exhibit high capacity values which are close to the theoretical ones. 9,10-Anthraguinone (AQ) (Figure 1a) is an example which shows a high utilization ratio during the first discharge process;^[8] however, the electrode using AQ itself significantly deteriorates during cycling. One of the reasons for this deterioration is the dissolution of the redox-related organic molecules into the electrolyte solutions.[18-20] To improve the cycling stability, suppressing the dissolution should be inevitable. While the applications of some special binder,^[21] separator,^[22] and

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Figure 1. Chemical structures of (a) 9,10-anthraquinone (AQ), (b) the AQ-dimer, and (c) the AQ-trimer.

2. Results

(a)

2.1. Synthesis

The AQ-dimer and trimer connected by the acetylene unit were synthesized by a palladium-catalyzed cross-coupling reaction (Figure 2). The trimethylsilylethynyl-anthraquinone (Me₃Si–C=C–AQ) was first synthesized by the reaction between bromo-anthraquinone and trimethylsilylacetylene. A hydrolysis reaction in an alkaline solution then gave the ethynyl-anthraquinone (H–C=C-AQ).^[26] The NMR and IR spectra of these compounds are shown in Figures S1-S4. A further coupling reaction between the obtained ethynyl-anthraquinone and mono-bromo-anthraquinone produced the dimer (AQ–C=C–AQ). The reaction between ethynyl-anthraquinone and di-bromo-anthraquinone formed the

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trimer (AQ–C≡C–AQ–C≡C–AQ). These newly synthesized oligomers were almost insoluble in the ordinary organic solvents at room temperature (Figure S5). This insolubility is important to realize long cycle-life active materials; however, it becomes difficult to apply normal solution-based purification techniques at the same time. While the obtained powders might include some impurities, analytical measurements, such as MS, IR, and Raman, supported the fact that the synthesized compounds have the desired structures which contain the anthraquinone structure connected by the triple bond (Figures S6–S9). Based on the SEM and XRD measurements, the obtained powders of the oligomers were found to have needle-like forms and are crystalline (Figures S9 and S10).



Figure 2. Synthetic routes for the AQ-dimer and AQ-trimer; reagents and conditions: (i) Me₃SiC≡CH, CuI, Pd(PPh₃)₂Cl₂, THF, i-Pr₂NH, reflux; ii) KOH *aq.* MeOH, THF (iii) 2-bromoanthraquinone, Pd(PPh₃)₂Cl₂, CuI, THF, *i*-Pr₂NH reflux; (iv) 2-ethynylanthraquinone, CuI, Pd(PPh₃)₂CI, THF, *i*-Pr₂NH, reflux.

2.2. Initial battery behavior

The AQ-monomer showed the initial discharge capacity of 219 mAh g⁻¹ with the average voltage of 2.3 V vs. Li_(C.E.) and the prepared dimer and trimer also showed similar values during the initial discharge process (AQ-dimer: 193 mAh g⁻¹, 2.3 V vs. Li_(C.E.); AQ-trimer: 214 mAh g⁻¹, 2.2 V vs. Li_(C.E.)) (Figure 3). The observed capacities are close to their theoretical values (AQ-dimer: 245 mAh g⁻¹, AQ-trimer: 241 mAh g⁻¹), suggesting that a two-electron transfer-type redox reaction of the AQ unit also takes place in the dimer and trimer. (The charge curves are omitted from this figure for visual clarity. Instead, they are depicted in Figure S11a along with their high-rate capability result in Figure S11b.) In the CV measurement (Figure S12), all the electrodes using the AQ monomer, dimer, and trimer showed two redox wave pairs, which also implies the above-mentioned two-electron transfer-type redox reaction.



Figure 3. First discharge curves of the electrodes containing the AQ-monomer (----) (blue dashed line), AQ-dimer (----) (green dotted dashed line), and AQ-trimer (---) (red solid line).

2.3. Cycle test

Figure 4 compares the cycling performance of the prepared electrodes. The capacity degradation of the monomer was fast, as previously reported;^[8,18-20] the electrode maintained only 14 mAh g⁻¹ after 100 cycles. At the same time, the cycle behaviors of the dimer and trimer were better, *i.e.*, the dimer and trimer exhibited 60 and 184 mAh g⁻¹ after 100 cycles, respectively. In particular, the capacity decay of the trimer was very low during the cycling.



Figure 4. Capacity retention behavior of the electrodes (AQ-monomer: Δ ; AQ-dimer: \Box ; AQ-trimer: \circ).

2.4. Quantum chemistry calculations

To understand the initial discharge behaviors of the AQ derivatives, DFT calculations were performed. Figure 5 compares the calculated energy levels of these derivatives along with the shapes of the related unoccupied molecular orbitals. The energy levels of the LUMOs of the dimer and trimer are 0.3 and 0.4 eV lower than that of the monomer, respectively. This estimation implies that these oligomers should show higher redox potentials than the monomer during the redox process related to the LUMO level. This result qualitatively agrees with the

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Figure 5. The calculated energy level diagrams of some MOs of the AQ-monomer, AQ-dimer, AQ-trimer, and the shapes of the MOs related to the discharge process.

discharge voltage values of these derivatives observed in the actual battery test; the dimer and trimer showed about 0.1 and 0.2 V higher redox voltages, respectively, during the early stage of the discharge process. Also, their association structures were investigated to understand the intermolecular interaction. Our calculations suggested parallel displaced stacking structures for a series of the AQ oligomers, shown in Figure 6, with the intermolecular distance of about 3.3 Å which is slightly underestimated but close to the interlayer distance of 3.4 Å for graphite. (As for this π -stack distance, a basis-set dependence was observed, i.e., a higher cost basis-set tends to give a longer and more accurate distance.) The calculated off-set π -stack geometry is often observed in the crystal structures of mconjugated ring systems. Furthermore, the calculated stacking configuration of the AQ-monomer is very similar to the reported crystallographic result,^[27] verifying this calculation approach. The obtained binding energy for the AQ-monomer was about 35 kJ mol⁻¹, which is a typical value for such stacked small molecules. As for the oligomers, higher values were obtained; i.e., 80 and 125 kJ mol⁻¹ for the AQ-dimer and trimer, respectively. These values are much higher than the stabilization energy of a small molecule association due to the usual van der Waals interaction.

Figure 6. The calculated stacking structures of (a) the AQ-monomer, (b) AQdimer, and (c) AQ-trimer.

3. Discussion

In order to use low-molecular-weight compounds for rechargeable batteries, improving their cycling stability is an important concern. As described in many reports, the discharge capacities of the electrodes using such small molecules tend to significantly decrease during cycling. The chemical stability of the active materials during cycling is surely important, and some papers suggested that introducing some protecting groups into the redox active moieties has a positive effect for prolonging the cycle-lives. Furthermore, the dissolution of redox active molecules into the electrolyte solution is considered to be one of the critical issues for their fast capacity degeneration. As to this point, we previously reported that there is a negative correlation between the solubility of the active materials and the cycling stabilities by comparing the benzoquinone derivatives carrying alkoxy groups; i.e., the lower the solubility in the solvent, the longer the cycle-life.^[28] To suppress the solubility of organic molecules, polymerization is an

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option which has been utilized by many scientists^[1-5] although the obtainable capacities sometimes become far lower than the theoretically expected ones. The introduction of polar groups is also an effective way to decrease the solubility in organic solvents. While some papers explain that polar organic active materials tend to show a long cycle-life,^[12,17,29] their theoretical capacities become low due to the heavy polar substituents. In addition, the direct fusion of the redox sites has been suggested to be effective for improving the cycling life performance;^[20,30] however, it often causes a voltage drop during the discharge process due to an intramolecular interaction.

In this study, the cycle-life of the electrode using the AQ-monomer was not long compared to those of the oligomers. The incorporated triple bond unit might work as a protecting group to improve the chemical stability during cycling; however, we consider that the observed differences in the cycle-lives are related to their solubility. In fact, the AQ-monomer is moderately soluble in the typical electrolyte solutions.^[20] On the other hand. the AQ-dimer and trimer are, as already described, insoluble in the ordinary organic solvents at least in the fully oxidized states (auinone states). Although the solubility difference between the dimer and trimer is not clear under ambient conditions, we suspect that the larger trimer has a stronger attractive intermolecular force than the dimer, thus the former would be less soluble than the latter. Our theoretical calculation supported this hypothesis. Intermolecular forces represented by the van der Waals forces are considered to be very weak in general; however, the calculated stacking energy value of 125 kJ mol⁻¹ for the trimer is much higher than the binding energy of the hydrogen bonding (10–40 kJ mol⁻¹), which is a relatively strong intermolecular force, and comparable to the level of covalent bonding (100-300 kJ mol⁻¹). This calculation indicates that oligomerization is an effective way to enhance the intermolecular attractive interaction, which should contribute to suppressing the dissolution.

4. Conclusions

A dimer and trimer with the anthraquinone (AQ) skeleton connected by a triple bond (-C=C-) were newly synthesized and their battery performance was compared to that of the AQmonomer. While the capacity of the AQ-monomer quickly decayed upon cycling, the synthesized oligomers showed improved behaviors. In particular, the trimer showed the best cycling performance; it retained an almost constant capacity during the one hundred cycles. This result indicated that the oligomerization of the soluble redox active molecular units is effective to extend the cycle-life without lowering the discharge voltage. A theoretical quantum chemistry calculation indicated that the intermolecular attractive interaction through the π - π interaction can become high enough by the oligomerization to stabilize the molecule in the crystal, which should contribute to suppressing the dissolution. Our finding in this study will be a quide to design a novel organic compound showing a high capacity and good cycling performance.

Experimental Section

Synthesis

(2-bromoanthraquinone, The starting materials 2,6dibromoanthraquinone,trimethylsilylacetylene) and the catalvsts (dichlorobis(triphenylphosphine)palladium(II) (Pd(PPh₃)₂Cl₂), copper iodide (Cul)) were purchased from reagent companies and used without further purification. The synthesized materials were characterized by ¹H-NMR (500 MHz), infrared (IR), and Raman spectroscopies, mass spectrometry (ASAP or MALDI), melting points measurement, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2-Trimethylsilylethynyl-9,10-anthraquinone: This precursor was synthesized by the coupling reaction of 2-bromoanthraquinone and trimethylsilylacetylene according to the literature.^[26] M.p.: 169°C. ¹H-NMR (400 MHz, CDCl₃, TMS): δ =8.36 (d, 1H, J=2 Hz), 8.32-8.28(m, 2H), 8.24 (d, 1H J=8 Hz), 7.84-7.78 (m, 3H), 0.30 (s, 9H). MS (ASAP), *m/z*. 305 [*M*+H]⁺. IR (powder), cm⁻¹: 2959 (-TMS), 2158 (C=C), 1677 (C=O).

2-Ethynyl-9,10-anthraquinone: This compound was prepared by hydrolysis of the above-mentioned trimethylsilylethynylanthraquinone in a quantitative yield.^[26] M.p.: 211°C. ¹H-NMR (400 MHz, CDCl₃, TMS): δ = 8.41 (d, 1H, J=2 Hz), 8.32 (t, 2H, J=5 Hz), 8.28 (d, 1H J=10 Hz), 7.87 (dd, 2H, J=2, 10 Hz), 7.85-7.80 (m, 2H), 3.38 (s, 2H). MS (ASAP), *m/z*. 233 [*M*+H]⁺. IR (powder), cm⁻¹: 3269 (ethynyl-H), 2111 (C=C), 1677 (C=O).

Bis(9,10-anthraquinone-2-yl)acetylene (AQ-dimer): A mixture of 2bromoanthraquinone (0.20 g, 0.70 mmol), 2-ethynylanthraquinone (0.16 g, 0.67 mmol), Cul (6.7 mg, 0.035 mmol), and Pd(PPh₃)₂Cl₂ (25 mg, 0.036 mmol) in tetrahydrofuran (40 mL) with diisopropylamine (4 mL) was stirred and heated at refluxing temperature for 15 h under a nitrogen atmosphere. After evaporating the solvents, the residue was washed with several organic solvents. The title compound was obtained as a yellow solid. Yield: 0.19 g, 63%. M.p.: 277°C (dec.). MS (ASAP/MALDI), *m/z*: 438 [*M*]⁻. IR, cm⁻¹: 1671 (C=O). Raman, cm⁻¹: 2194 (C=C).

2,6-Bis((9,10-anthraquinone-2-yl)ethynyl)-9,10-anthraquinone (AQtrimer): This trimer was prepared by the coupling reaction between 2,6dibromoanthraquinone (0.12 g, 0.32 mmol) and 2-ethynylanthraquinone (0.15 g, 0.62 mmol) under conditions similar to those used for the synthesis of the AQ-dimer. The title compound was obtained as a brown solid. Yield: 0.10 g, 47%. M.p.: 321°C (dec.). MS (ASAP/MALDI), m/z 668 [M]⁻. IR, cm⁻¹: 1675 (C=O). Raman, cm⁻¹: 2186 (C=C).

Electrodes and cells

The active material powder, conductive additive (acetylene black), and binder (polytetrafluoroethylene) were mixed in the weight ratio of 4:5:1 to make a sheet. The positive electrode was prepared by pressing the sheet onto an aluminum mesh current collector. Each electrode was adjusted to contain about 3.00 mg of the active material. IEC R2032 coin-type cells were assembled with the prepared sheet-type positive electrode, a lithium metal negative electrode, a glass filter as the separator, and the electrolyte solution which contained lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in diglyme (1 mol L^{-1}).

Charge/discharge test

The prepared cells were first galvanostatically discharged (*i.e.*, the reduction of the positive electrode) at the current density of 20 mA g^{-1} with respect to the active materials with a cut-off voltage of 1.5 V vs. Li_(C.E.),

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then charged (*i.e.*, the oxidation) at the same current density with a cut-off voltage of 3.0 V vs. Li_(C.E.). The charge/discharge test was conducted at 30°C using an electrochemical measurement instrument (ABE system, Electrofield Co., Ltd.). The capacity values are described in terms of the mass of the active material in this paper.

Quantum chemistry calculations

To obtain a theoretical insight into the charge/discharge behaviors of the organic materials, the density functional theory (DFT) calculations were performed using the GAUSSIAN 03 ^[31] and GAUSSIAN 09 packages.^[32] The geometry of the active material molecules was optimized at the B3LYP/6-31G(d) level. The shapes of the calculated molecular orbitals (MOs) were drawn using Gauss View 3.0.^[33] Also, to estimate the intermolecular interactions among the molecules, a single point calculation based on the Møller–Plesset perturbation theory at the MP2/6-31G(d) level for the coupled molecule coordinates which were optimized by a DFT method using the BHandH functional at the same level.

Conflict of Interest

The authors declare no conflict of interest.

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Keywords: Lithium ion battery • Long cycle-life • Oligomerization • Organic Cathode • π - π interaction

- [1] P. Novák, K. Müller, S.V. Santhanam, O. Hass, Chem. Rev. 1997, 97, 207-281.
- [2] M. Armand, J.M. Tarascon, *Nature* **2008**, *451*, 652–657.
- [3] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* 2002, 359, 351-354.
- [4] H. Wang, S. Yuan, D. Ma, X. Huang, F. Meng, X. Zhang, Adv. Energy Mater. 2014, 4, 1301651.
- [5] T. Sun, Z. Li, H. Wang, D. Bao, F. Meng, X. Zhang, Angew. Chemie. Int. Ed. 2016, 128, 10820-10824.
- [6] H. Yoshikawa, C. Kazama, K. Awaga, M. Satoh, J. Wada, Chem Commun. 2007, 0, 3169-3170.
- [7] H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J.M. Tarascon, *ChemSusChem* 2008, 1, 348-355.
- [8] Z. Song, H. Zhan, Y. Zhou, Chem. Commun. 2009, 4, 448-450.
- [9] T. Matsunaga, T. Kubota, T. Sugimoto, M. Satoh, *Chem. Lett.* 2011, 40, 750-752.
- [10] Y. Inatomi, N. Hojo, T. Yamamoto, S. Watanabe, Y. Misaki, *ChemPlusChem* 2012, 77, 973-976.
- [11] Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato, T. Takui, *Nat. Mater.* 2011, *10*, 947-951.
- [12] A. Shimizu, H. Kuramoto, Y. Tsujii, T. Nokami, Y. Inatomi, N. Hojo, H. Suzuki, J. Yoshida, J. Power Sources 2014, 260, 211-217.
- [13] T. Yokoji, H. Matsubara, M. Satoh, J. Mater. Chem. A 2014, 2, 19347-19354.
- [14] T. Sun, Z. Li, X. Zhang, Research 2018, Article ID 936735.
- [15] H. Wang, S. Yuan, Z. Sia, X. Zhang, *Energy Environ. Sci.* 2015, *8*, 3160-3165.

- [16] M. Yao, H. Senoh, S. Yamazaki, Z. Siroma, T. Sakai, K. Yasuda, J. Power Sources 2010, 195, 8336-8340.
- [17] M. Yao, M. Araki, H. Senoh, S. Yamazaki, T. Sakai, K. Yasuda, *Chem. Lett.* 2010, 39, 950-952.
- [18] M. Yao, H. Senoh, K. Kuratani, T. Sakai, T. Kiyobayashi, *ITE-IBA Lett.* 2011, 4, 53-56.
- [19] M. Yao, H. Senoh, T. Sakai, T. Kiyobayashi, Int. J. Electrochem. Sci. 2011, 6, 2905-2911.
- [20] M. Yao, S. Yamazaki, H. Senoh, T. Sakai, T. Kiyobayashi, *Mater. Sci. Eng. B* 2012, 177, 483-487.
- [21] T. Ma, Q. Zhao, J. Wang, Z. Pan, J. Chen, Angew. Chem. Int. Ed. 2016, 55, 6428–6432.
- [22] C. Wang, C. Jiang, Y. Xu, L. Liang, M. Zhou, J. Jiang, S. Singh, H. Zhao, A. Schober, Y Lei, *Adv. Mater.* **2016**, *28*, 9182-9187.
- [23] K. Zhang, C. Guo, Q. Zhao, Z. Niu, J. Chen, Adv. Sci. 2015, 2, 1500018.
- [24] J.M. Tour, Acc. Chem. Res. 2000, 33, 791-804.
- [25] M. Mayor, H.B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer, Angew. Chem. Int. Ed. 2003, 42, 5834-5838.
- [26] R.A.I. Abou-Elkhair, T.L. Netzel, Nucleosides Nucleotides Nucleic Acids 2005, 24, 85-110.
- [27] M. Slouf, J. Mol. Struct. 2002, 611, 139-146.
- [28] M. Yao, H. Ando, T. Kiyobayashi, Energy Procedia 2013, 34, 880-887.
- [29] M. Yao, T. Numoto, M. Araki, H. Ando, H.T. Takeshita, T. Kiyobayashi, Energy Procedia 2014, 56, 228-236.
- [30] M. Yao, H. Ando, T. Kiyobayashi, Energy Procedia 2016, 89, 222-230. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. [31] Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanavakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.01 (2004), Gaussian, Inc., Wallingford, CT.
- [32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01 (2010), Gaussian, Inc., Wallingford, CT.
- [33] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W.L. Hovell and R. Gilliland (2003), GaussView, Version 4.1.2, Semichem, Inc., Shawnee Mission, KS.

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The cycle-life of organic active materials was found to be extended by oligomerization. While the capacity of the electrode using the anthraquinone monomer quickly decreased, the ones of its oligomers showed a longer cyclelife. Theoretical calculations indicted that the intermolecular binding energy is increased to the level of covalent bonding by oligomerization, which would be beneficial to overcome the dissolution problem during cycling.

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