



Electron-deficient anthraquinone derivatives as cathodic material for lithium ion batteries



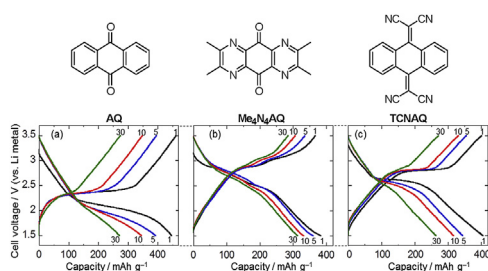
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HIGHLIGHTS

- We studied the electronic/structural properties of electron-deficient AQ derivatives.
- Design principles for Li-ion batteries using AQ derivatives as cathode were obtained.
- Differences of Li coordination and structure of AQ greatly affect battery properties.
- Me₄N₄AQ showed a high charge/discharge voltage with high cyclability.

GRAPHICAL ABSTRACT



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ABSTRACT

We studied the electronic and structural properties of electron-deficient anthraquinone (AQ) derivatives, Me₄N₄AQ and TCNAQ, and investigated their charge-discharge properties in lithium ion batteries along with those of AQ. Cyclic voltammogram, X-ray structure analysis and theoretical calculations revealed that these three acceptors have different features, such as different electron-accepting properties with different reduction processes and lithium coordination abilities, and different packing arrangements with different intermolecular interactions. These differences greatly affect the charge-discharge properties of lithium ion batteries that use these compounds as cathode materials. Among these compounds, Me₄N₄AQ showed a high charge/discharge voltage (2.9–2.5 V) with high cyclability (>65% of the theoretical capacity after 30 cycles; no decrease after 15 cycles). These results provide insight into more in-depth design principles for lithium ion batteries using AQ derivatives as cathodic materials.

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1. Introduction

Rechargeable batteries play a major role as a power supply for electronic devices and their importance has increased because of their potential applications as storage devices in the field of ecological and/or renewable energy. Lithium ion batteries have

traditionally been used in portable electronic devices due to their low weight and high energy density [1]. However, since current lithium ion batteries use rare metals such as cobalt for cathode electrode, large-scale fabrication would increase the unit cost, cause environmental pollution, and be limited by scarcity of resources. Thus, redox active organic materials have attracted much attention due to their abundance, even from natural sources, low cost and suitability for use in lightweight flexible devices. Both organic anodic and cathodic materials have been extensively studied. For example, polyacetylene [2], organic sulfur compounds [3], trioxotriangulene [4], and bipolar porous polymeric frameworks [5] have been investigated for their potential as organic

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cathodic materials. Despite these extensive studies on the development of organic electrode materials, there is still a great need for compounds that exhibit fast charge-discharge processes with high repeatability and high output properties. Although the dissolution of organic cathode active materials into the electrolyte has been a problem for cell performance [6], small redox active π -molecules are still promising candidates for use in lithium ion batteries because the use of such small organic molecules should increase the theoretical capacity.

Herein we investigated organic cathodic materials with high terminal voltage based on *p*-benzoquinone derivatives. Electronic active benzoquinones [7] and 7,7,8,8-tetracyano-*p*-quinodimethane derivatives are promising candidates for organic cathode materials, and have been extensively investigated, including with respect to their polymeric materials [8]. Their low molecular weights and two-electron reduction processes enable their high theoretical capacity. Thanks to the versatility of organic materials, their electronic properties can be easily controlled by the introduction of electron-donating and/or electron-accepting substituents and/or extension of the π -conjugation core. It is preferable to use low molecular weight materials composed of light atoms in the second row of the periodic table due to their high energy density and ready availability, and the sustainability of the cell. Thus, we focused on tetramethyltetraazaanthraquinone (Me₄N₄AQ) [9] and tetracyanoanthraquinodimethane (TCNAQ) [10] (Fig. 1). Fusion of the two electron-accepting pyrazine rings to *p*-benzoquinone forms a Me₄N₄AQ molecule, which should show much higher electron-accepting ability than *p*-benzoquinone. Since electron affinity and charge/discharge voltage are strongly correlated in benzoquinone derivatives [11], Me₄N₄AQ should serve as a good cathodic material with high output voltage/capacity. Although the preparation of Me₄N₄AQ derivatives has been reported [9], there have been no studies on its photophysical, electrochemical, or crystallographic properties, or on its application to rechargeable batteries. TCNAQ has been investigated as a strong electron-acceptor [10] and its use in the formation of a charge-transfer complex [10j], electrochromic materials [10k], and photochemical reaction [10l] has already been reported. Since it is a strong electron-acceptor, TCNAQ is also a good candidate for use as a cathodic material. Another interesting feature of this molecule is the dynamic structural transformation that is shown upon two-electron reduction. The quinone derivatives that have been examined so far for use as a cathode material have not shown such dynamic structural changes during the redox process. Therefore, the effect of this dynamic structural change on the electron-transfer reaction would be an interesting subject of research regarding the capacitor properties of TCNAQ. Herein, we report the electronic, structural, and charge-discharge properties of Me₄N₄AQ and TCNAQ as cathodic materials in lithium ion batteries, in comparison to those of anthraquinone (AQ) as a reference compound (Fig. 1).

2. Experimental section

2.1. Materials

Commercially available AQ was used in the experiments as received. Me₄N₄AQ and TCNAQ were prepared as reported in the literature [9,10h]. Me₄N₄AQ was synthesized by the condensation reaction of tetraamino-*p*-benzoquinone with diacetyl, and was purified by recrystallization from CHCl₃/EtOH. TCNAQ was prepared by the condensation reaction of anthraquinone with malononitrile in the presence of TiCl₄, and was purified by recrystallization from AcOH. The purity of the materials was assessed by elemental analysis.

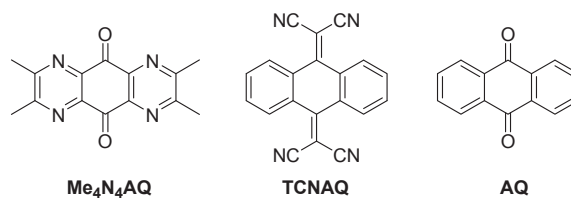


Fig. 1. Molecular structures of Me₄N₄AQ, TCNAQ and AQ.

2.2. X-ray crystallographic analysis

Single crystals of Me₄N₄AQ suitable for x-ray crystallographic analysis were grown from MeOH. Crystallographic data were collected using a Rigaku RAPID-II diffractometer equipped with a rotating anode fitted with a multilayer confocal optic using Cu-K α ($\lambda = 1.54187 \text{ \AA}$) radiation. Structure refinement was carried out using the full-matrix least-squares method on F^2 . Calculations were performed using the Crystal Structure and SHELEX [12] software packages. Parameters were refined using anisotropic temperature factors except for the hydrogen atom.

2.3. Crystal data for Me₄N₄AQ

C₄₆H₅₂N₆, M 688.96, triclinic *P*-1, $a = 8.9013(2)$, $b = 13.2462(3)$, $c = 13.2462(3) \text{ \AA}$, $\alpha = 84.1372(7)$, $\beta = 81.9146(7)$, $\gamma = 68.2867(7)^\circ$, $V = 1920.21(6) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.191 \text{ g cm}^{-3}$, $\mu = 5.426 \text{ cm}^{-1}$, number of measured reflections = 22122, number of independent reflections = 6897, number of reflections used = 6897, $R = 0.0831$, $R_w(F^2) = 0.2827$, GOF = 1.113. Crystallographic data for Me₄N₄AQ was deposited at The Cambridge Crystallographic Data Centre (CCDC). CCDC 1484422 contains the crystallographic data, which is available free of charge by CCDC at <http://www.ccdc.cam.ac.uk>.

2.4. Photophysical and electrochemical analyses

UV–vis spectra were measured in CH₂Cl₂ with a Perkin-Elmer LAMBDA 750 spectrophotometer. Cyclic voltammetry measurements were performed with a Yanako P-1100 in a 0.1 M Bu₄NBF₄ solution of CH₂Cl₂. All of the redox potentials were obtained as E/V vs a Ag/AgCl reference electrode at a scan rate of 100 mV s⁻¹.

2.5. Theoretical calculations

Geometry optimizations and normal mode calculations for isolated molecules of AQ, Me₄N₄AQ and TCNAQ in the vacuum state were performed at the B3LYP/6-31G(d) level using the Gaussian 09 program package [13]. Calculations of intermolecular transfer integrals (t 's) were performed with the PW91 functional and Slater-type triple- ζ plus polarization (TZP) basis sets using the ADF (Amsterdam Density Functional) package [14,15]. Atomic coordinates from the crystal structure of Me₄N₄AQ and those from previously reported data for AQ [16] and TCNAQ [10i] were used to calculate the overlap integrals.

2.6. Preparation of electrodes and battery cells

Electrodes were prepared as described below. Activated carbon (AC; Maxsorb[®], KANSAI COKE CHEMICALS COMPANY) was dispersed in AQ-dissolved acetone, Me₄N₄AQ-dissolved chloroform and TCNAQ-dissolved THF, respectively, and organic solvents were removed under a vacuum. Quinone-supported AC was mixed with polyethylene oxide (PEO, MW = 4.0 $\times 10^6$; Wako Pure Chemical Industries, Ltd) and lithium bis(trifluoromethylsulfonyl)amide

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