COMMUNICATION

Switching of the π-electronic conjugations in the reduction of a dithienylethene-fused p-benzoquinone†

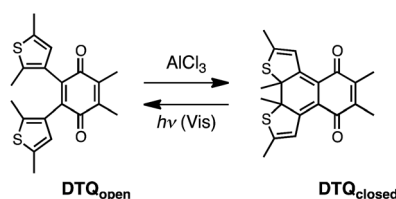Eiji Saito, Takumi Ako, Yasuhiro Kobori* and Akihiko Tsuda*

The electron accepting character of a dithienylethene-fused p-benzoquinone derivative is significantly reduced upon ring-closing isomerization. Visible light unlocks the π-electronic conjugation of the quinone so it can be utilized for a light-driven oxidation reaction.

Quinones, an oxidized species of aromatic compounds, play important roles in biological systems, and are also valuable in industry. They serve as electron acceptors, oxidizing agents, dyes, and pigments in biochemistry and organic chemistry.[1–5] The electrochemical properties and chemical reactivity of quinone are dependent on its substituent groups, and are also affected by solvent and external chemical stimuli.[6] Many examples have been reported of controlling the reactions of quinones through weak interactions with additives such as metal ions.[7] We previously reported supramolecular [4 + 2] cycloaddition and [2 + 2] photocycloaddition reactions of a p-benzoquinone derivative bearing an oligoether side-chain that can bind a metal ion through electrostatic interaction.[8,9] The bound metal ion reduces or increases the π-electron density of the quinone, changing its reactivity in both thermal and photochemical reactions. However, to the best of our knowledge, physical operation of the chemical reactions of quinone with the light is an unprecedented subject. The light-driven chemical reactions, which allow for arbitrary control of specific target and time, promise new developments in photoresponsive reagents and catalysts, photoconductive materials, and focal reactions in living organisms and nanomaterials.[10–12] In the present study, we report a light-driven oxidation reaction with a dithienylethene-fused p-benzoquinone, which unlocks the π-electronic conjugation of the quinone upon exposure to visible light.

Katsumura and coworkers reported synthesis of dithienylethene-fused p-benzoquinones using the Stille's type Pd(0) catalyzed coupling reaction.[13] The ring-opening and -closing reactions of their derivatives were then reported by Liebeskind and coworkers.[14] The ring-opening quinones cause ring closure on photolysis. However, the observed conversion in the photostationary state (PSS) is only 5–30%, and is also dependent on the substituent groups attached to the quinone and thiophene groups. The conversion is increased through an acid-promoted ring-closing reaction with $AlCl_3$, $FeCl_3$, or CF_3SO_3H in the dark, and the ring-closing isomer can be isolated in yields of up to 95% through column chromatography. Although the observed differences in absorption spectra between the ring-opening and -closing forms indicate significant changes in the π-electronic conjugations, there are no reports that focus on their electron accepting character and chemical reactivity. Knowing this, we herein studied redox properties of a dithienylethene-fused quinone **DTQ** by means of cyclic voltammetry and EPR spectroscopy together with theoretical calculations, and applied it to a light-driven chemical reaction (Scheme 1).

We synthesized **DTQ** in line with the literature.[13,14] The molecular structure of ring-opening **DTQ$_{open}$** was characterized by means of ^1H and ^{13}C NMR and electronic absorption spectroscopies, mass spectrometry, and X-ray crystallography (Fig. S1 and Table S1†).[15] When **DTQ$_{open}$** was mixed with 3 equiv. of $AlCl_3$ in CH_2Cl_2, it was converted immediately to the

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Scheme 1 Ring-closing and -opening reactions of **DTQ** with $AlCl_3$ and visible light, respectively.

ring-closing isomer **DTQ$_{closed}$**. Through chromatographic separation, it was isolated in 71% yield (Fig. S2†). The sample solutions of **DTQ$_{open}$** and **DTQ$_{closed}$** showed orange and reddish violet with λ_{max} in the lowest energy absorption band at 446 and 520 nm with the molar absorption coefficient of 1750 and 5941 $M^{-1}\,cm^{-1}$, respectively (Fig. 1). These spectral data then allowed estimation of the ratio of **DTQ$_{open}$** and **DTQ$_{closed}$** in the solution. When a cyclohexane solution of **DTQ$_{open}$** was exposed to 320 nm UV-light with a 500 W xenon lamp for 20 min, the spectral change due to photoisomerization occurred, and 26% conversion to **DTQ$_{closed}$** was evaluated in the photostationary state (PSS) (Fig. S3†). On the other hand, **DTQ$_{closed}$** showed quantitative conversion to **DTQ$_{open}$**, when exposed to visible light (>380 nm) (Fig. S4†). The quantum yield (Φ) of this ring-opening reaction upon excitation at 420 nm was determined to be 0.78,[16] which is larger than that of diarylethene derivatives reported previously.[17] However, without photo-irradiation, no isomerization occurred when a sample solution of **DTQ$_{closed}$** was left for 14 days in the dark at room temperature (Fig. S5†). This is the characteristic P-type feature of diarylethene. The sample solution, thus, reversibly changes the absorption spectrum upon photo-irradiation with visible and UV light (Fig. S6†).

The reduction potentials of **DTQ$_{open}$** and **DTQ$_{closed}$** in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 as a supporting electrolyte were measured by cyclic voltammetry (Fig. 2). The ring-opening **DTQ$_{open}$** showed two redox couples at $E_{1/2} = -1.24$ V and -2.01 V ($vs.$ Fc/Fc$^+$), which may correspond to **DTQ$_{open}$**/**DTQ$_{open}$**$^{\cdot-}$ and **DTQ$_{open}$**$^{\cdot-}$/**DTQ$_{open}$**$^{2-}$, respectively. This is a characteristic redox profile observed in quinone compounds. On the other hand, the ring-closing **DTQ$_{closed}$** showed a negatively shifted one redox peak at $E_{1/2} = -1.80$ V. Plots of E_{pa} and E_{pc} values with respect to the square root of the scan rate ($v^{1/2}$) in the range of 50–500 mV s^{-1} provided a potential difference $\Delta E_p = 57.9$ mV (Fig. S7†). Since ΔE_p should be $59/n$ mV, where n is the number of electrons, at 25 °C in an ideal Nernstian process,[18] the observed redox couple was assigned as a 1e$^-$ transition. The observed large negative shift of the reduction potential in **DTQ$_{closed}$** may originate in the fact that its radical anion, including 1,4-semidion, does not undergo aromatic stabilization upon a one-electron reduction.[19]
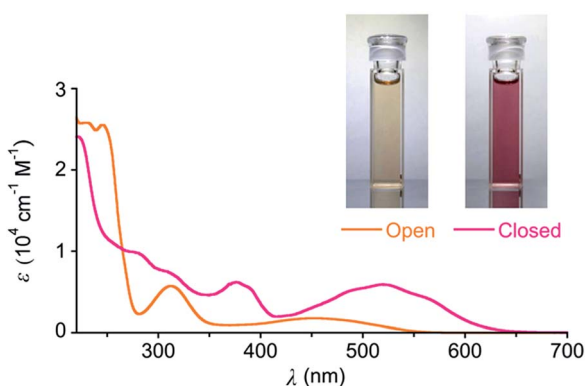

Fig. 2 Redox profiles in cyclic voltammetry (V $vs.$ Fc/Fc$^+$) of mixtures of **DTQ$_{open}$** and **DTQ$_{closed}$** in CH_2Cl_2. Scan rate, 100 mV s^{-1}; working electrode, Pt; supporting electrolyte, 0.1 M Bu_4NClO_4.

We then demonstrated EPR spectroscopy for the reduced forms of **DTQ$_{open}$** and **DTQ$_{closed}$**. With a sample solution prepared upon mixing **DTQ$_{open}$** and metallic sodium in CH_2Cl_2 at room temperature, the EPR signal was observed at $g = 2.005$ with hyperfine splitting most likely due to methyl protons attached at 5,6-positions (Fig. 3a). The hyperfine coupling constant (hfc) was estimated to be $a(6H) = 1.59$ G by a computer-simulated spectrum of **DTQ$_{open}$**$^{\cdot-}$ with the DFT calculation at UB3LYP/6-311+G(d,p) level.[20] The sample solution prepared upon mixing **DTQ$_{closed}$** and metallic sodium also provided the EPR signal at $g = 2.005$ (Fig. 3b). However, the observed hyperfine structure was entirely different from that of **DTQ$_{open}$**$^{\cdot-}$, and was simulated by applying to the three hfcs $a(6H) = 1.20$ G, $a(6H) = 1.11$ G, and $a(2H) = 0.39$ G (Fig. 3b). The

Fig. 1 Photos and UV–Vis absorption spectra of cyclohexane solutions of **DTQ$_{open}$** and **DTQ$_{closed}$** at 20 °C. The spectra were taken on the concentration at 4.0×10^{-5} M.
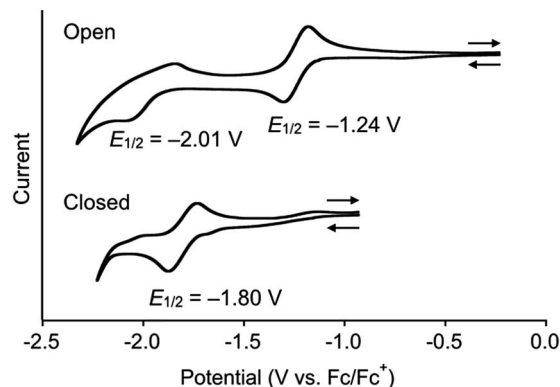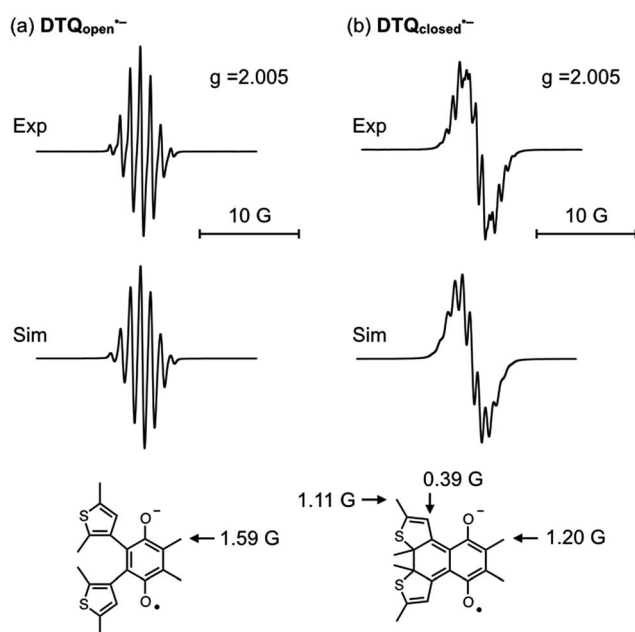

Fig. 3 EPR spectra of (a) **DTQ$_{open}$**$^{\cdot-}$ and (b) **DTQ$_{closed}$**$^{\cdot-}$ generated upon mixing **DTQ** with metallic sodium in deaerated CH_2Cl_2 with the computer simulation spectra and the hyperfine coupling constants. The spectral measurements were demonstrated at room temperature.

result indicates contributions of β-protons on the thiophene rings and methyl protons attached to the quinone and thiophene rings in the spectrum. The spin density distributions of **DTQ$_{open}$**$^{\bullet-}$ and **DTQ$_{closed}$**$^{\bullet-}$ were then calculated by DFT program (Fig. S8†). It showed that spin density of **DTQ$_{open}$**$^{\bullet-}$ is distributed mainly on the quinone moiety, especially at the carbonyl oxygens. This result would explain the observed hfc in EPR spectrum. On the other hand, the calculated spin density of **DTQ$_{closed}$**$^{\bullet-}$ is only slightly distributed on the thiophene rings, but is concentrated at unsaturated 1,4-diketone moiety. This does not agree with the fact that its EPR spectrum, as described above, indicates that there should be a reduced contribution of the quinone moiety with the adding of contributions from thiophene groups to the observed hfcs in Fig. 3b. However, we found that this disagreement can be reasonably explained by the frontier MOs and the orbital energies calculated for **DTQ$_{closed}$** (Fig. 4). The calculation showed that **DTQ$_{closed}$** has two nearly degenerated LUMO and LUMO+1 levels with a small energy gap of 0.07 eV. The LUMO has larger coefficients of the atomic orbitals in the quinone moiety, while LUMO+1 has them in both the quinone and the thiophene rings. The observed three different hfcs of **DTQ$_{closed}$**$^{\bullet-}$ is well characterized with the orbital character of LUMO+1 of **DTQ$_{closed}$**. Hence, the contribution of the degenerated LUMO+1, which provides larger distribution of the spin onto the thiophene rings, in the formation of its anion radical, may allow delocalization of the radical over the components. Conclusively, in **DTQ$_{open}$**, where the attached thiophene groups adopt almost perpendicular conformation, the quinone moiety undergoes an aromatic stabilization by forming a semiquinone radical anion, as in the case of usual quinones. However, such an aromatic stabilization is not expected in **DTQ$_{closed}$**$^{\bullet-}$, because its planar structure allows orbital delocalizations over the entire molecule with an antibonding π* character between the quinone and thiophene moieties in LUMO and in LUMO+1 (Fig. 4). This is coincident with the above-mentioned negatively shifted redox peak at $E_{1/2}$ = −1.80 V and with the three hfcs in the EPR spectrum (Fig. 2 and 3b, respectively).

The electrochemical properties of the ring-opening and -closing **DTQ** revealed by the above experiments prompted us to expect different reactivity in their chemical reductions. Considering their one-electron reduction potentials described above, we investigated a possible hydrogen exchange reaction between **DTQ** and tetramethylhydroquinone **Me$_4$HQ**, a reduced form of tetramethyl-*p*-benzoquinone **Me$_4$Q** (Fig. 5).[21] Judging from the reduction potential of **Me$_4$Q** [$E_{1/2}$ = −1.40 V (*vs.* Fc/Fc$^+$)], which is lower than that of **DTQ$_{open}$**, but is higher than that of **DTQ$_{closed}$**, we expected the reaction (Fig. S9†). The reaction was demonstrated in CDCl$_3$ at room temperature, and monitored by ^{1}H NMR spectroscopy. When the ring-opening **DTQ$_{open}$** was mixed with **Me$_4$HQ**, its ^{1}H NMR peaks disappeared, and two sets of new peaks appeared with other peaks corresponding to tetramethyl quinone **Me$_4$Q** (Fig. S10†). Since 2D-NMR spectroscopies of the isolated product actually provided two sets of the correlation profiles (Fig. S11†), and further, its elemental analysis and mass spectral profile were consistent with those calculated for the reduced **DTQ** (Fig. S12†), the peaks may be originated from the mixture of anti- and parallel conformational isomers of the reduced **DTQ$_{open}$** (**DTHQ**).[22] The product was thus reconverted quantitatively to **DTQ$_{open}$** upon oxidation with Ag$_2$O (Fig. S13†). In sharp contrast to the result with **DTQ$_{open}$**, interestingly, no reaction was observed with **DTQ$_{closed}$** even upon mixing with 10 equiv. amounts of **Me$_4$HQ** (Fig. 5). With these results in mind, we then demonstrated a possible light-driven oxidation reaction of **Me$_4$HQ** with **DTQ$_{closed}$**. When the sample solution, which showed no reaction in the dark, was exposed to visible light
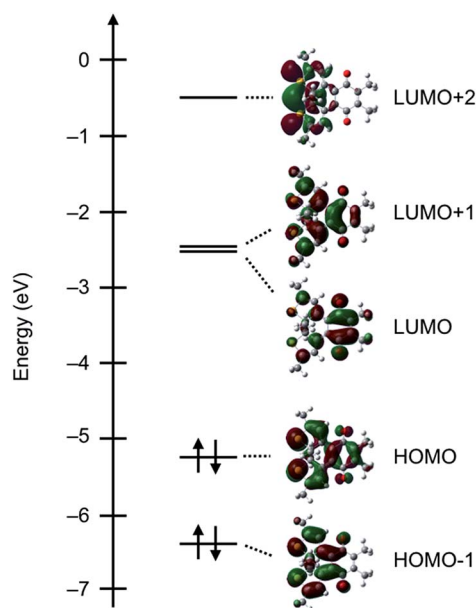

Fig. 4 Calculated frontier MOs and the orbital energies of DTQ$_{closed}$ in DFT with B3LYP/6-311G(d,p) level. Red and green colors indicate the positive and negative orbitals, respectively.
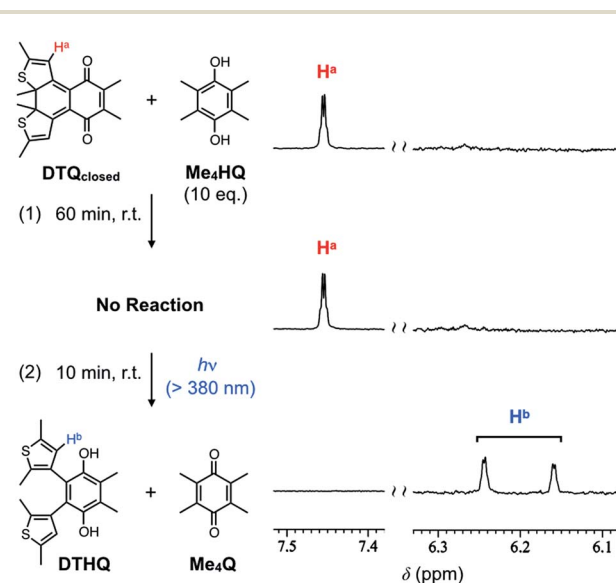

Fig. 5 ^{1}H NMR spectral profiles for a 1 : 10 mixture of DTQ$_{closed}$ and Me$_4$HQ after (1) stirring of the sample solution for 60 min in the dark and (2) photoirradiation with visible light for 10 min at room temperature.

(>380 nm) for 10 min, a hydrogen-exchange reaction occurred to give **DTHQ** in quantitative yield (Fig. 5). Here, the photo-conversion from **DTQ$_{closed}$** to **DTQ$_{open}$** most likely triggered this reaction. The results can be explained by the order of first reduction potentials in cyclic voltammetry (**DTQ$_{open}$** > **Me$_4$Q** > **DTQ$_{closed}$**), which may correlate with the thermal stability of the semiquinone radical, a possible intermediate in the formation of the corresponding hydroquinone.

Conclusions

In this study, we found that a dithienylethene-fused *p*-benzo-quinone derivative **DTQ** changes its electronic properties dramatically through ring-opening and -closing isomerizations. Both isomers underwent one-electron reduction to give the corresponding anion radicals. The spectral studies together with DFT calculations indicate that **DTQ$_{open}$**$^{•-}$ adopts semi-quinone form, while **DTQ$_{closed}$**$^{•-}$ allows spin delocalization between quinone and thiophene groups. The electron accepting character as well as oxidizability of **DTQ$_{closed}$** is reduced significantly in comparison with that of **DTQ$_{open}$**. Visible light unlocks the π-electronic conjugation of the quinone in **DTQ** utilizing it for a light-driven oxidation reaction.

Acknowledgements

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