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Switching of Redox Properties Triggered by Thermal Equilibrium between Closed-shell Folded and Open-shell Twisted Species

Yusuke Ishigaki,^{*[a]} Takumi Hashimoto,^[a] Kazuma Sugawara,^[a] Shuichi Suzuki,^[b] and Takanori Suzuki^{*[a]}

In memory of Keiji Okada (1951-2019) and Toshio Mukai (1924-2020)

Abstract: Thermally switchable redox properties have been reported to be due to a change in the spin state of newly designed overcrowded ethylenes, which can adopt closed-shell folded and open-shell twisted forms. In this paper, tetrathienylanthraquinodimethane derivatives were designed to be in thermal equilibrium between a more stable folded form and less stable but more donating twisted diradical in solution, so that the oxidation potential can be controlled by heating/cooling. This is the first example of a switching of redox properties based on a thermally equilibrated twisted diradical, which can be more easily oxidized to the twisted dication.

Highly strained molecules have attracted much attention from the viewpoint of their unique structural and physical properties. For example, overcrowded ethylenes (OCEs), in which the C=C double bond is surrounded by bulky substituents, have been widely investigated regarding their configurational aspects. Normal alkenes have a planar geometry, whereas OCEs are forced to adopt a folded (F) and/or twisted (T) form, the latter of which, in general, has a higher HOMO and a lower LUMO than the former. Due to the large difference in the electronic structure (e.g., the T-form has a smaller HOMO-LUMO gap), their dynamic structural change is accompanied by a change in physical properties, and thus many studies on OCEs have been devoted to developing chromic materials^[1-4] and molecular switches.^[5-8] As exemplified by bianthrone (I)^[9,10] and bithioxanthylidenes (II),^[11,12] which are classified as bistricyclic aromatic enes (BAEs) (Figure 1a), in many cases the F-form is more stable than the corresponding T-form by about 5-20 kcal mol⁻¹.

We envisaged that, by reducing the energy difference (ΔE) between the F- and T-forms, both forms could be present and in thermal equilibrium at ambient temperature. The contribution of the less stable form can be controlled by changing the temperature, so that the redox properties of OCEs can be switched by heating/cooling in solution, which has not yet been realized. To make the twisted-structures more stable, a promising approach would involve reduction of the π -bond order

of the C=C double bond by insertion of quinodimethane units, as in Chichibabin's hydrocarbons, which have been explored in detail for their open-shell diradical characters, although they are not OCEs (Figure 1a).^[13-16] Thus, insertion of anthraquinodimethane (AQD) unit(s) would make the twisted-structures favored for the extended OCEs (e.g. III),^[17,18] regardless of whether the electronic nature is T-form (closed-shell) or D-form (open-shell diradical form). Both of these would have a much smaller HOMO-LUMO gap than the F-form (*vide infra*), and not only the electronic structure but also the spin state would be controlled when the F- and D-forms are thermally equilibrated in properly designed OCEs.

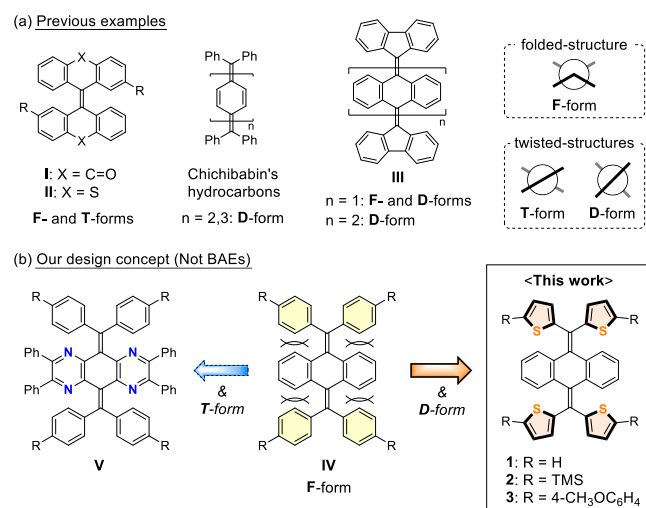


Figure 1. a) Previous examples. b) Molecular design for this study.

Although the F-form of 11,11,12,12-tetraarylanthraquinodimethanes (IV)^[4] is far more stable than the corresponding twisted-structures (Table S1), we recently found that the T-form is more favored for tetraazaanthraquinodimethane derivatives (V),^[19] in which all inner C-H groups at the fjord region on the AQD core of IV are replaced by nitrogen atoms. Thus, slight modification of the molecular structure of IV would reduce the ΔE between the F- and twisted-structures, and the marginal decrease in steric repulsion around C=C double bonds may favor twisted-structures (both T- and D-forms). Based on this background, we considered that we could access the twisted-structures in thermal equilibrium with the F-form under the proper molecular design. Thus, AQD derivatives 1-3 with four 2-thienyl rings (Figure 1b), a new type of OCE, have been designed with the expectation that they would exist as an equilibrated mixture of F-

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and **D**-forms and exhibit a facile conformational change under heating/cooling in solution. Furthermore, the latter has a higher HOMO level and could be more easily oxidized than the former. Herein, we demonstrated that a certain contribution from the thermally excited triplet diradical for methoxyphenyl derivative **3** could induce the reversible switching of redox properties upon heating/cooling based on the temperature-controlled contribution of the **D**-form.

Before the synthetic study, density functional theory (DFT) calculations were conducted for AQD derivatives **1-3**. According to this DFT study [(U)B3LYP/6-31G*], several conformers assignable to the **F**-form, closed-shell **T**-form, and open-shell diradicals (**D-s** for singlet state and **D-t** for triplet state) were obtained (Figure 2). In the parent compound **1**, the **F**-form is the most stable state, as in many other AQDs, yet the twisted-structures (**T**-, **D-s**-, and **D-t**-forms) are very close in energy. By attachment of substituents, the ΔE can be modified to be very small, especially in methoxyphenyl derivative **3**. As expected, compared to the **F**-form, higher HOMO- and lower LUMO-levels were calculated for the twisted-structures, and the orbital energies of these three twisted species (**T**-, **D-s**-, and **D-t**-forms) were close to each other regardless of their spin states for all cases of **1-3** (Table S2 and Figures S1-S3).

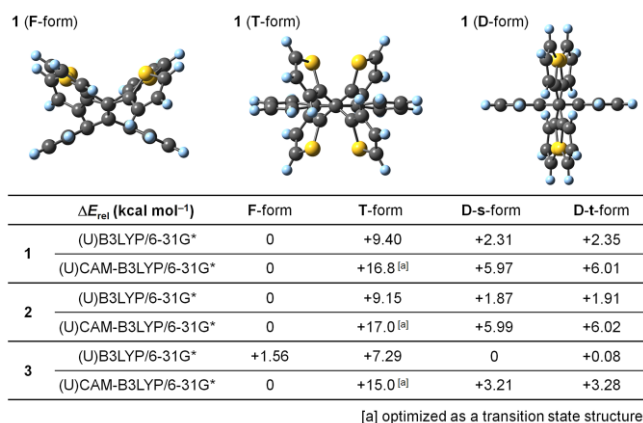
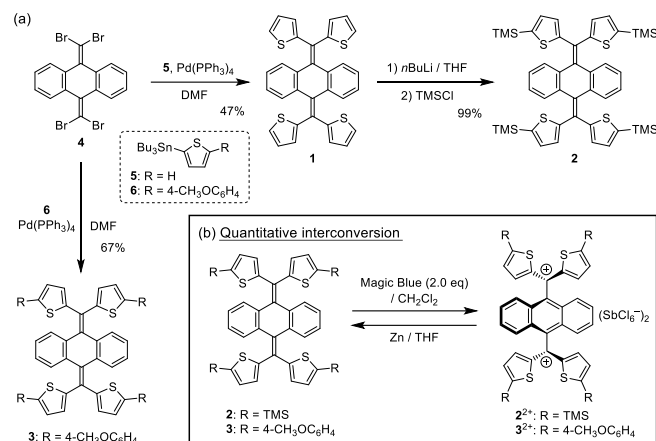


Figure 2. Optimized structures of **1** based on DFT calculations [(U)B3LYP/6-31G*]. Relative energies of **1-3** are summarized.

The target compounds **1** and **3** were prepared as stable solids by using the cross-coupling reaction of **4** with the corresponding thienyl stannanes (Scheme 1a). TMS derivative **2** was obtained in 99% yield by treatment of **1** with *n*BuLi followed by the addition of TMSCl. X-ray analyses revealed that all compounds adopt the **F**-form in crystals (Figures 3a-c). The butterfly-shaped **F**-forms of **1-3** closely resemble those of previously reported AQD derivatives.^[4] Thanks to the electron-donating nature of the dithienylmethylene group,^[20] when **2** and **3** were treated with two equivalents of (4-BrC₆H₄)₃N⁺SbCl₆⁻ (Magic Blue), the dication salts **2**²⁺(SbCl₆⁻)₂ and **3**²⁺(SbCl₆⁻)₂ were obtained quantitatively (Scheme 1b) whereas **1**²⁺ could not be isolated. When the dications **2**²⁺ and **3**²⁺ were reduced by Zn powder, the neutral species **2** and **3** were recovered quantitatively. The crystal structures of dications **2**²⁺ and **3**²⁺

were identified by X-ray analyses and the results showed that both dications adopt almost orthogonally twisted structures (Figures 3d,e). Thus, it is most probable that the most stable geometry in the neutral state is the **F**-form, whereas the dication prefers the perpendicular geometry as in the **D**-form.



Scheme 1. a) Preparation scheme for **1-3**. b) Redox interconversions between **2**²⁺ and **3**²⁺.

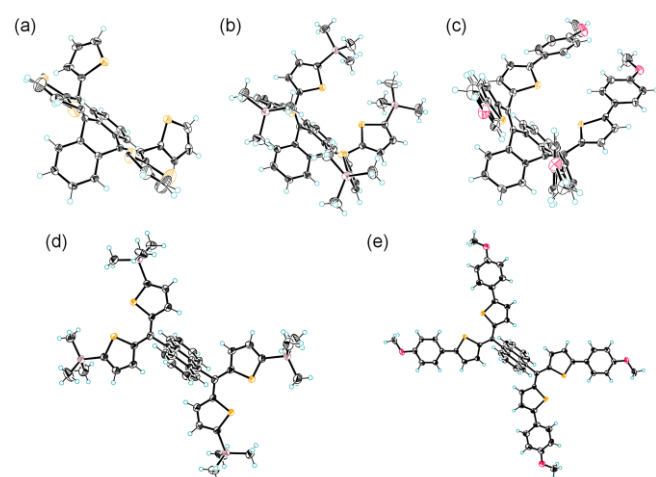


Figure 3. ORTEP drawings of a-c) **1-3**, d) **2**²⁺, and e) **3**²⁺. Solvent molecules and counterions are omitted for clarity.

Cyclic voltammetry for **1** in CH₂Cl₂ exhibits one-wave-two-electron redox peaks at quite different potentials for the oxidation of **1** and the reduction of **1**²⁺, respectively (Figure 4 and Table 1). The large separation between oxidation and reduction waves is due to a change in structure between folded species and perpendicular dications, classified as dynamic redox (*dyrex*) systems.^[21] This is also the case for TMS derivative **2**. However, a reversible redox wave was observed for **3** at 297 K, with a cathodic shift of the oxidation wave compared to **1** and **2**, suggesting that **3** and **3**²⁺ adopt a similar structure in CH₂Cl₂. This result indicates that the neutral species **3** in solution is oxidized when it adopts one of the twisted-structures,

because its dication 3^{2+} cannot adopt any other conformation except the perpendicularly twisted structure.

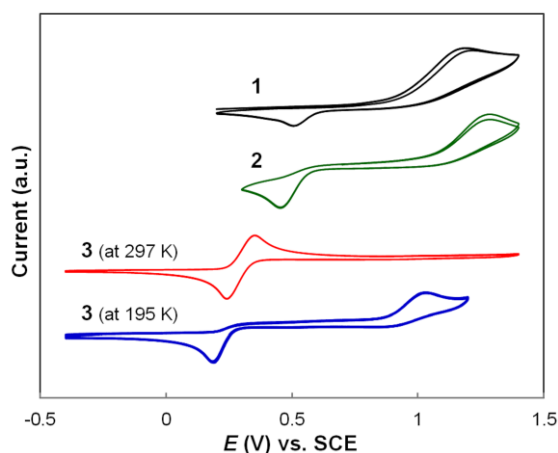


Figure 4. Cyclic voltammograms of 1-3 at 297 K and 3 at 195 K in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 .

Table 1. Redox potentials for 1-3.

Compds.	Temp. (K)	E^{ox} (V)	E^{red} (V)
1/1 $^{2+}$	297	+1.19 ^[a]	+0.51 ^[a]
2/2 $^{2+}$	297	+1.29 ^[a]	+0.45 ^[a]
3/3 $^{2+}$	297		+0.30
3/3 $^{2+}$	195	+1.03 ^[a]	+0.19 ^[a]

[a] For the irreversible waves, peak potentials are shown as E^{ox} and E^{red} .

We envisaged that folded- and twisted-structures of **3** should be in thermal equilibrium. To validate this hypothesis, we carried out cyclic voltammetry at 195 K in CH_2Cl_2 . As expected, the voltammogram showed *dyrex* behavior, indicating that only the folded form is present in solution at 195 K, and thus a large structural change between neutral donor and dication was observed (Figure 4). Therefore, this is the first example of the complete switching of redox behavior based on thermal equilibrium between folded- and twisted-structures, although the voltammograms of previously reported redox-active OCEs exhibit both processes corresponding to the oxidation of folded- and twisted-structures.^[11,12,22,23]

To investigate the conformational details of methoxyphenyl derivative **3**, we conducted variable-temperature (VT) ^1H NMR analyses. Resonances assigned to a single C_{2v} -symmetric species appeared upon cooling to 193 K in CD_2Cl_2 (Figure 5), i.e., AQD derivative **3** could adopt the **F**-form as the most stable conformer at lower temperatures. In contrast, at higher temperatures in $\text{DMSO}-d_6$ (Figure S4), significant broadening of

NMR signals was observed, probably due to an increase in the population of thermally excited triplet diradical (**D-t**-form).

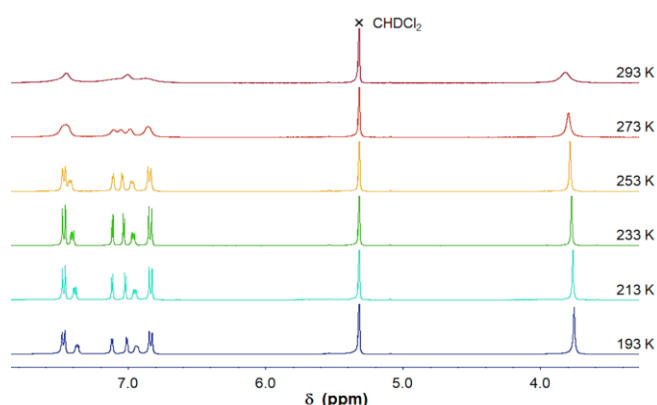


Figure 5. VT-NMR spectra of **3** in CD_2Cl_2 .

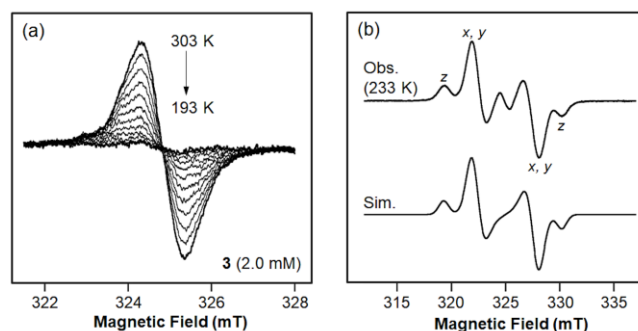
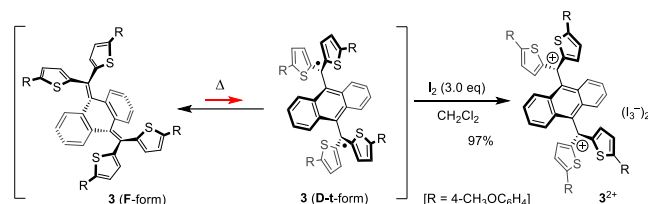


Figure 6. a) VT-ESR spectra of **3** in CH_2Cl_2 . b) Observed and simulated ESR spectra of **3** in benzophenone (1.0 wt%). $|D/h\nu| = 0.0051 \text{ cm}^{-1}$; $|E/h\nu| \sim 0 \text{ cm}^{-1}$; $g_x = g_y = 2.003$, $g_z = 2.004$.

In voltammetric and VT-NMR analyses, the presence of twisted-structures for **3** was fully clarified by the experimental results. We then focused on whether the twisted-structures would be the **T**-form (closed-shell) or **D**-form (open-shell). Electron spin resonance (ESR) measurement of **3** obviously showed a broad signal assignable to open-shell species (Figure 6a). Upon cooling to 193 K, the ESR signal disappeared, which also supported the notion that methoxyphenyl derivative **3** adopts the closed-shell **F**-form at lower temperatures (Figure S5). Thus, the open-shell species is present in solution in thermal equilibrium with the **F**-form. Furthermore, the ESR spectrum of **3** in a frozen-solution state at 233 K, whose sample was prepared from melted benzophenone solution by rapid cooling, clearly displayed signals typical of triplet species (Figure 6b). The spin-centers distance was estimated to be 8.0 Å by the point-dipole approximation using the D value; this value is in good agreement with the calculated spin structure of **D-t**-form (Figure S3). These results demonstrated that the **D-t**-form of **3** is present in the solution even at ambient temperature.

The open-shell **D**-form can undergo two-electron oxidation more easily than the closed-shell **F**-form to produce twisted

dication 3^{2+} , which represents a very rare example of thermally equilibrated species that actually switches the molecular properties. Previously, Magic Blue was used to oxidize **3** to 3^{2+} , however, the **D**-form generated by thermal equilibrium has a higher HOMO than the **F**-form. Thus, **3** could be oxidized by a weak oxidant such as I_2 based on their oxidation potentials.^[24] In fact, the dication salt $3^{2+}(I_3^-)_2$ was obtained quantitatively by the addition of three equivalents of I_2 to the CH_2Cl_2 solution of **3**, meaning that the **D**-form was certainly oxidized by I_2 and supplied by rapid equilibration as a result of the facile change in structure (Scheme 2).



Scheme 2. Oxidation of thermally equilibrated **3** (**D**-form) with I_2 .

In conclusion, we synthesized AQD derivatives **1-3** with two dithienylmethylene groups, where we expected the coexistence of and rapid conformational change between folded- and twisted-structures. The substituents on the thienyl group can adjust the energy difference between the folded **F**-form and twisted **D**-form. VT analyses and ESR measurements revealed that the methoxyphenyl derivative **3** is in thermal equilibrium between the closed-shell **F**-form and the open-shell **D**-form at higher temperatures, whereas the **F**-form exists predominantly at lower temperatures. As a result, not only redox behavior but also magnetic properties^[25] could be controlled reversibly by changes in a thermal stimulus.

Acknowledgements

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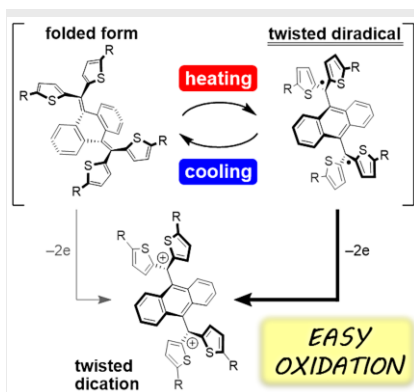
Keywords: Redox chemistry • Cations • Radicals • Thermal equilibrium

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Entry for the Table of Contents

COMMUNICATION

Oxidation potentials can be switched reversibly by heating/cooling in solution due to a change in the spin state of anthraquinodimethane derivatives. This is a quite rare example of switchable redox properties based on a thermally equilibrated twisted diradical, which can be oxidized more easily than the folded form.



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