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Author(s)	Noro, Karin; Tani, Ayano; Tadokoro, Tomoki et al.
Citation	Journal of organic chemistry, 90(36), 12727-12733 https://doi.org/10.1021/acs.joc.5c01545
Issue Date	2025-09-12
Doc URL	https://hdl.handle.net/2115/98075
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Type	journal article
File Information	Ishigaki et al., J. Org. Chem. 2025, 90, 12727-12733.pdf



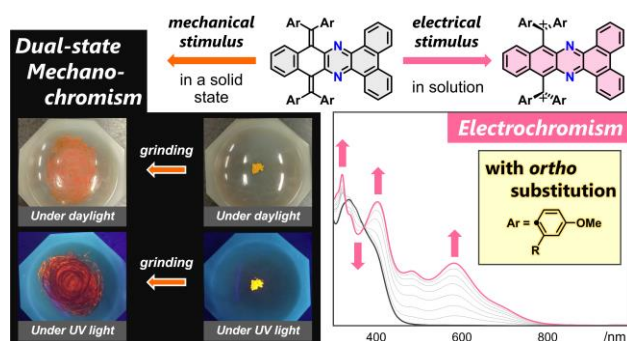
Dual-State Mechano- and Electrochromic Responses Enabled by Sterically Strained Diazaanthraquinodimethanes

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KEYWORDS: strained molecules, redox systems, UV–vis–NIR spectroscopy, mechanochromism, electrochromism



ABSTRACT: Stimuli-responsive materials with reversible optical properties are of significant interest for the development of functional systems. Herein, we present the design and synthesis of diazaanthraquinodimethane (N₂AQD) derivatives incorporating *ortho*-substituted 4-methoxyphenyl groups. A phenanthrene-fused scaffold was employed to balance conformational flexibility and redox stability, while an *ortho*-substitution strategy was used to control molecular conformation and near-infrared (NIR) absorption. Whereas neutral donors and their corresponding dications exhibit folded and twisted conformations, respectively, a greater steric strain by introducing *ortho* substituents induces structural deformation that can lead to effective conjugation and enhanced switching ability. Thus, the *ortho*-dimethyl-substituted derivative showed red-shifted absorption in both neutral and dicationic states. Mechanochromic behavior was observed in a solid state, involving both ground-state (color) and excited-state (emission) changes, which is due to a crystal-to-amorphous phase transition. Additionally, reversible electrochromism was demonstrated in solution. These results highlight N₂AQDs as promising platforms for multifunctional chromic materials responding to mechanical and electrical stimuli.

Introduction

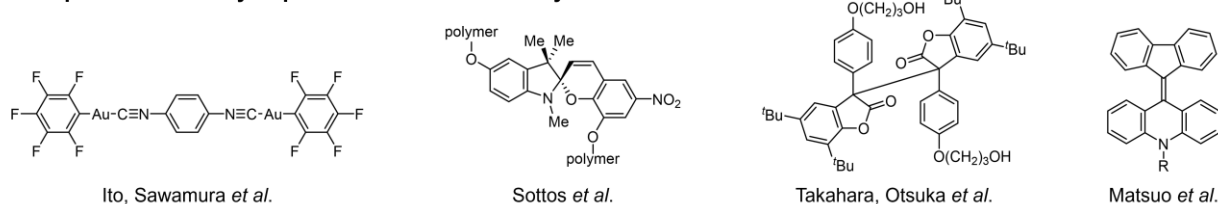
Materials capable of reversibly switching their physical properties in response to external stimuli have garnered significant attention due to their broad applicability in advanced functional systems. Among these, chromic phenomena, where a stimulus induces a reversible change in color, have been extensively explored for use in environment-responsive sensors and smart materials.^{1,2} Electrochromism, one of the chromic phenomena, wherein a reversible change in color is induced by electrical input.^{3–6} Thus, electrochromic systems are widely implemented in applications such as display materials and smart windows,^{7–11} and are recognized as a prominent example of stimulus-responsive systems. For these applications, inorganic electrochromic materials have been predominantly employed due to their high durability and long-term stability.^{8–11}

In contrast, organic electrochromic compounds offer distinct advantages, including facile modulation, fine tunability, and potentially lower cost and environmental impact, particularly by avoiding the use of rare and/or heavy metals.^{12–17} In organic electrochromic systems, color changes are typically associated

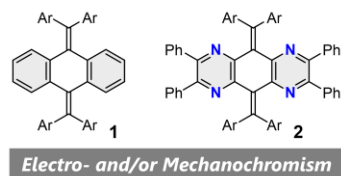
with redox processes that generate charged and radical species upon application of an electric potential. The formation of an open-shell species is often detrimental to reversibility and thus represents a significant limitation in the design of organic-based electrochromic systems. To construct reversible electrochromic molecules, stabilizing the radical species is of great importance. Another approach is that avoiding the generation of long-lived open-shell species. Indeed, we have studied dynamic redox (*dyrex*) systems, where not only color but also molecular structure can be changed upon electron transfer.^{18,19} Thus, we have demonstrated that apparent even-electron oxidation processes, which minimize the concentration of reactive open-shell intermediates, can effectively overcome these limitations.^{20,21}

In addition to solution-phase chromic systems, increasing attention has been directed toward chromic responses in a solid state. For instance, mechanochromism, a phenomenon wherein mechanical stimuli induce reversible color changes, has emerged as a promising area of study.^{22–25} Such mechanochromism is often induced by changes in chemical bonds, intermolecular interactions, and/or molecular conformation in the

(a) Examples of Previously Reported Mechanochromic Systems



(b) Previous Study



(c) This Work

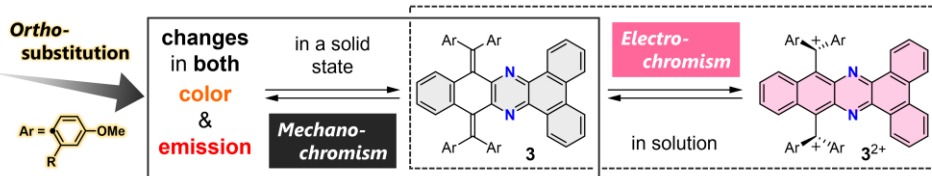


Figure 1. (a) Previous examples of mechanochromic systems. Mechano- and/or electrochromic systems: (b) our previous study and (c) this work. [3a: Ar = 4-MeOC₆H₄, 3b: Ar = 4-MeO-2-MeC₆H₃, 3c: Ar = 2-Cl-4-MeOC₆H₃, and 3d: Ar = 4-MeO-2,6-Me₂C₆H₃]

solid state (Figure 1a).^{26–33} Mechanochromic materials have been actively investigated for applications such as pressure-sensing systems.^{34–36}

Mechanochromism can be classified into two categories: (i) ground-state chromism, in which color changes under daylight, and (ii) excited-state chromism, in which emission color changes under excitation light source. However, the design concept of compounds that exhibit reversible and switchable mechanochromic behavior in both ground and excited states remains elusive.^{37,38} The development of such materials demands the establishment of a new molecular design concept, and represents a significant challenge and opportunity in the field of responsive organic materials.

Regarding the chromic systems, we reported two types of anthraquinodimethane (AQD)-based molecules (Figure 1b). One is tetraarylated AQD derivative **1** that exhibits two-way chromic behavior, e.g., excited-state mechanochromism in the solid state and electrochromism in solution,³⁹ while the other is nitrogen-containing AQD derivative **2** that displays a drastic change in both color and emission depending on the molecular conformation in the crystal, enabling the observation of both mechanochromism.⁴⁰ Thus, AQD-based frameworks hold great promise as scaffolds for developing multifunctional chromic systems, offering valuable guidelines for the design of advanced functional materials. However, there were no systems that exhibit mechanochromism in both ground and excited states and electrochromism. In this study, by tuning the quinodimethane core through the incorporation of an *ortho*-substitution strategy to enhance near-infrared (NIR)-absorbing properties,⁴¹ we designed compounds **3** and successfully achieved not only these mechanochromic responses but also electrochromism in the NIR region (Figure 1c). This work demonstrates a rational design approach for imparting a wide range of chromic functionalities.

Results and Discussion

To achieve both mechanochromic and electrochromic responses, flexibility of the molecular backbone and stability of the corresponding cationic species are of great importance. However, excessive flexibility may lead to undesired side reactions during redox processes. Therefore, to impart appropriate rigidity while maintaining mechanical-stimulus responsiveness,

we adopted a phenanthrene-fused diazaanthraquinodimethane (N₂AQD) framework as the central skeleton. Azaanthraquinodimethanes often undergo a ring-closure reaction in the oxidized state, however, the fused-phenanthrene moiety can suppress this reaction^{42,43} and thereby achieve electrochemical reversibility. Furthermore, since molecular conformation significantly influences absorption and emission properties, *ortho*-substituted derivatives were designed not only to enhance NIR absorption but also to enable conformational control. Based on these

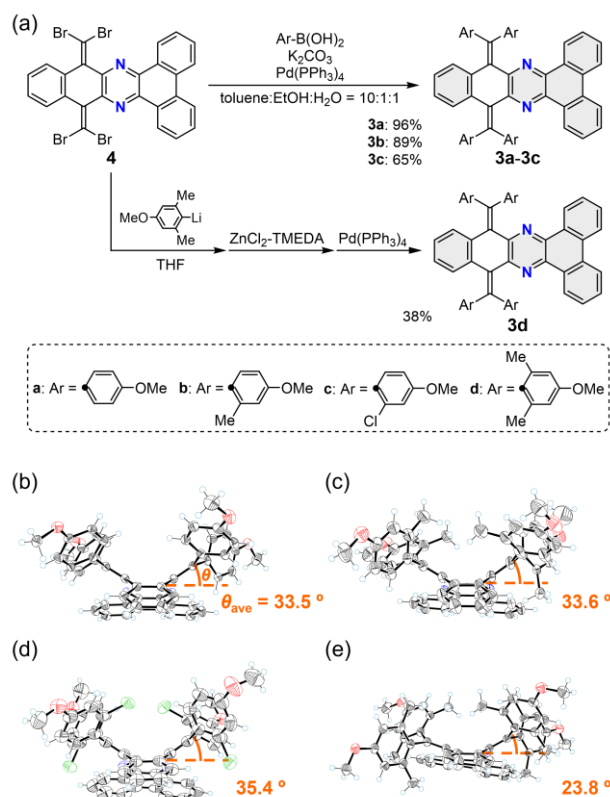


Figure 2. (a) Preparation of N₂AQD derivatives **3a–3d**. X-ray crystal structures (ORTEP drawings) of (b) **3a**, (c) **3b**, (d) **3c**, and (e) **3d** with the average bent angle θ_{ave} . Thermal ellipsoids are shown at 50% probability. Solvent molecules and disordered atoms are omitted for clarity. One of the two crystallographically independent molecules is shown for **3c**.

considerations, a series of AQD derivatives **3a–3d** was rationally designed.

As shown in Figure 2a, *ortho*-nonsubstituted N₂AQD **3a** with 4-methoxyphenyl groups was synthesized in 96% yield via Suzuki-Miyaura cross-coupling reaction of tetrabrominated precursor **4**⁴² with 4-methoxyphenylboronic acid. *Ortho*-monosubstituted derivatives **3b** and **3c**, with a methyl group and a chlorine atom at the 2-position on the 4-methoxyphenyl group, were prepared in respective yields of 89% and 65% in a similar manner. Meanwhile, via Negishi cross-coupling reaction, *ortho*-dimethyl-substituted N₂AQD derivative **3d** was synthesized in 38% yield. The vapor diffusion method gave nice single crystals suitable for X-ray diffraction analysis for all derivatives **3a–3d**. X-ray crystallographic analyses revealed that all N₂AQD derivatives **3** adopt a folded conformation (Figure 2b–e), as in typical AQD derivatives, e.g., **1**. The average bent angle θ_{ave} between the central plane, defined as the four carbon atoms, and the exomethylene moiety decreases in the *ortho*-dimethyl-substituted derivative **3d**, compared to those in other N₂AQDs **3a–3c** ($\theta_{\text{ave}}/^\circ$ = 33.5 for **3a**, 33.6 for **3b**, 35.4 for **3c**, and 23.8 for **3d**). This difference is attributed to the significantly greater steric strain in **3d** between the central backbone and aryl groups as well as between *gem*-aryl groups, which makes the exomethylene twisted (Figure S9 and Table S1). As a result of such skeletal deformation, **3d** exhibits longer-wavelength absorption in CH₂Cl₂ [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 387 (sh, 18500) and 335 (27600) for **3a**, 393 (sh, 14500) and 336 (22800) for **3b**, 390 (14600) and 325 (27800) for **3c**, and 424 (24600) and 361 (17800) for **3d**] (Figures S11 and S12 and Table 1). These

results were also supported by time-dependent density functional theory (TD-DFT) calculations at the CAM-B3LYP/6-31G* level (Figures S15 and S19 and Table S5).

We conducted cyclic voltammetry (CV) measurements to investigate the redox behavior of N₂AQD derivatives **3** (Figure 3). To obtain clearer voltammograms of each compound, dication salts, the preparation of which was shown later, were used for the measurements. Cyclic voltammograms of the dication salts of **3a**, **3b**, and **3c** in CH₂Cl₂ show two-electron (2e) reduction peaks ($E_{\text{p}}^{\text{red}}$) at +0.44, +0.65, and +0.93 V vs SCE, respectively. As a result of the large structural change characteristic of the dynamic redox (*dyrex*) systems,^{18,19} 2e-oxidation peaks, corresponding to the oxidation of neutral N₂AQDs, appeared in the far anodic region ($E_{\text{p}}^{\text{ox}}/\text{V}$ vs SCE = +0.83 for **3a**, +0.95 for **3b**, and +1.21 for **3c**). In contrast, *ortho*-dimethyl-substituted **3d/3d²⁺** exhibit reversible redox behavior ($E_{1/2}/\text{V}$ vs SCE = +0.77 for **3d/3d²⁺**). This is also accounted for by the partially twisted deformation of the quinodimethane skeleton, suggesting that the change in structure before and after redox reactions is quite small. In addition, the oxidation potential of **3d** is nearly identical to that of **1d** ($E_{1/2}/\text{V}$ = +0.72),⁴¹ indicating that the lowering of the HOMO level due to nitrogen incorporation is compensated by its elevation resulting from the π -extension through the introduction of the phenanthrene framework. The observed redox potentials for these derivatives were well reproduced by differential pulse voltammetry and DFT calculations (CAM-B3LYP/6-31G*), regardless of the presence or absence of *ortho* substituents (Figures S14 and S16).

Then, to investigate the redox interconvertible property of N₂AQD derivatives **3**, we conducted the chemical oxidation and reduction reactions on a preparative scale. The dication salts

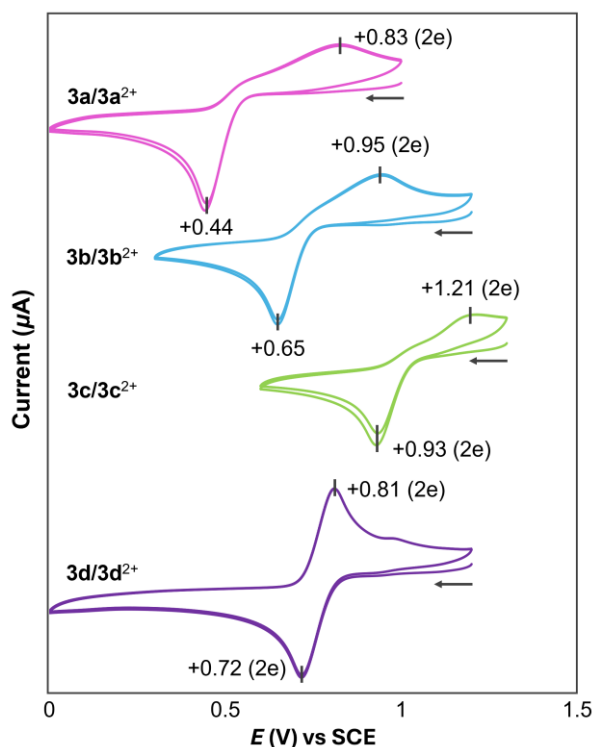


Figure 3. Cyclic voltammograms of dications (SbF₆[−] salts) of N₂AQD derivatives **3a–3d** (1 mM) in CH₂Cl₂ containing 0.1 M Bu₄NBF₄ as the supporting electrolyte at 298 K (scan rate: 0.1 V s^{−1}; Pt electrode). The initial potentials: +1.0 V (**3a²⁺**), +1.2 V (**3b²⁺**), +1.3 V (**3c²⁺**), and +1.2 V (**3d²⁺**), switching potential: 0 V (**3a²⁺**), +0.3 V (**3b²⁺**), +0.6 V (**3c²⁺**), and 0 V (**3d²⁺**), and the direction of initial scan (negative).

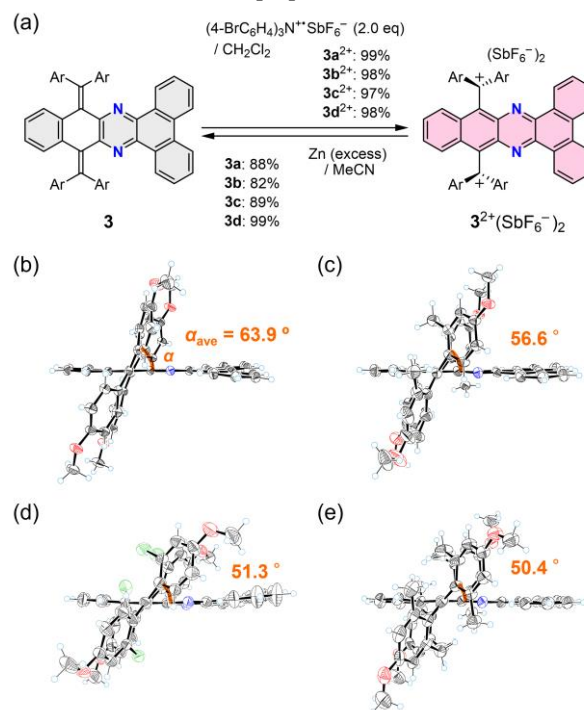


Figure 4. (a) Redox interconversion between N₂AQD derivatives **3a–3d** and their dication salts. X-ray crystal structures (ORTEP drawings) of (b) **3a²⁺**(SbF₆[−])₂, (c) **3b²⁺**(SbF₆[−])₂, (d) **3c²⁺**(SbF₆[−])₂, and (e) **3d²⁺**(SbF₆[−])₂ with the average twist angle α_{ave} . Thermal ellipsoids are shown at 50% probability. The counterions, solvent molecules, and disordered atoms are omitted for clarity.

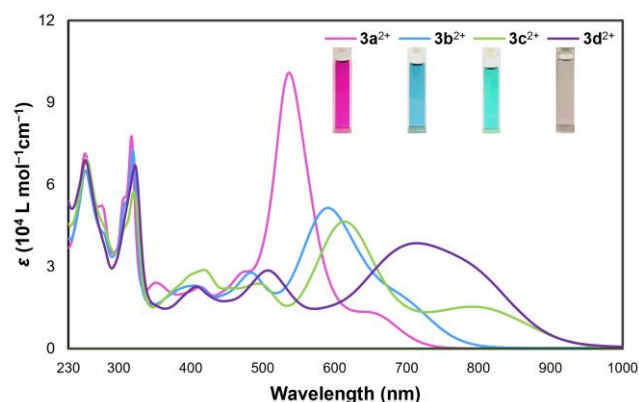


Figure 5. UV-vis-NIR spectra of $3a^{2+}(\text{SbF}_6^-)_2$ (magenta), $3b^{2+}(\text{SbF}_6^-)_2$ (blue), $3c^{2+}(\text{SbF}_6^-)_2$ (green), and $3d^{2+}(\text{SbF}_6^-)_2$ (violet) in CH_2Cl_2 .

$3a^{2+}(\text{SbF}_6^-)_2$ – $3d^{2+}(\text{SbF}_6^-)_2$ were synthesized and isolated quantitatively as stable entities by treatment of the neutral N_2AQD with two equivalents of $(4\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbF}_6^-$ (Figure 4a). The original N_2AQDs **3** were recovered by treatment of the dications with an excess amount of Zn powder. As in the cases of the neutral donors, single crystals suitable for X-ray diffraction analysis were obtained by the vapor diffusion method for all dication salts $3a^{2+}(\text{SbF}_6^-)_2$ – $3d^{2+}(\text{SbF}_6^-)_2$. X-ray crystallographic analyses revealed that all dications 3^{2+} adopt a twisted conformation (Figure 4b–e), as in typical AQD-based dications, e.g., 1^{2+} . Notably, all dications have a dibenzo-fused diazatetracene core, showing that heteroacene structure can also be formed upon oxidation of the corresponding heteroatom-embedded

Table 1. Photophysical data for N_2AQD derivatives **3** and corresponding dication salts $3^{2+}(\text{SbF}_6^-)_2$ in CH_2Cl_2 .

	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)		$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)
3a	387 (sh, 18500) 335 (27600)	3a²⁺	640 (13500) 537 (101000)
3b	393 (sh, 14500) 336 (22800)	3b²⁺	687 (20500) 591 (51500)
3c	390 (14600) 325 (27800)	3c²⁺	790 (15300) 614 (46400)
3d	424 (24600) 361 (17800)	3d²⁺	785 (31600) 714 (38500)

electron donors, as in recent studies.⁴⁴ A decrease in the average twist angle α_{ave} between the diarylmethyl moiety and the diazatetracene core was observed with increased steric strain by introducing *ortho* substituents ($\alpha_{\text{ave}}/^\circ = 63.9$ for $3a^{2+}$, 56.6 for $3b^{2+}$, 51.3 for $3c^{2+}$, and 50.4 for $3d^{2+}$). As a result of a lowered LUMO level due to the decreased twist angle α_{ave} , the SbF_6^- salts of the dications exhibit longer-wavelength absorptions in CH_2Cl_2 [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 640 (13500) and 537 (101000) for $3a^{2+}$, 687 (20500) and 591 (51500) for $3b^{2+}$, 790 (15300) and 614 (46400) for $3c^{2+}$, and 785 (31600) and 714 (38500) for $3d^{2+}$], and the color of the solution drastically changes (Figure 5 and Table 1). The relationship between molecular conformation and absorption property was also supported by (TD-)DFT calculations at the CAM-B3LYP/6-31G* level (Figures S17 and S20 and Table S6).

Based on the aforementioned results, we considered that N_2AQD **3** would undergo conformational changes induced by

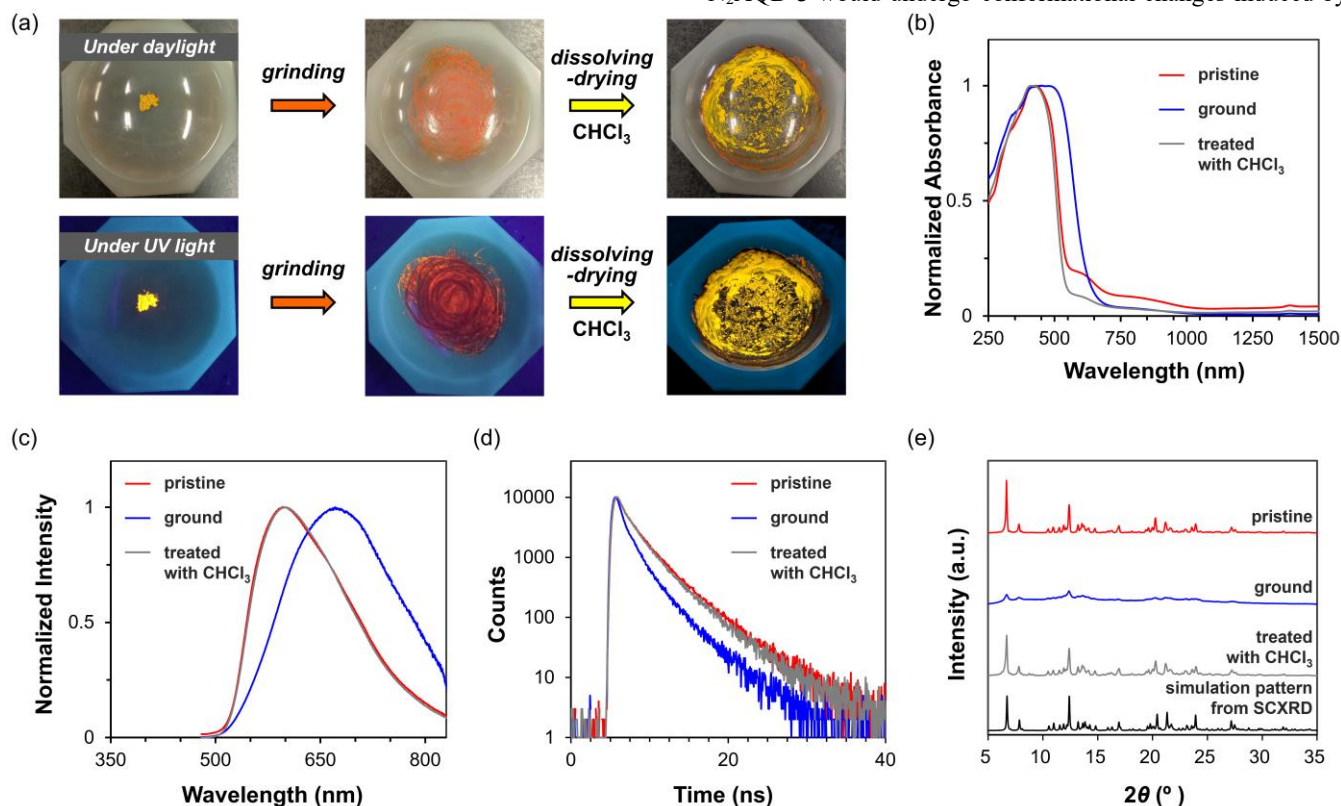


Figure 6. Dual-state mechanochromic behavior of **3d**. (a) Photographs of **3d** under daylight (upper) and UV light (lower) in various states. Changes in (b) diffuse reflectance and (c) emission spectra, (d) emission decay, and (e) PXRD pattern for pristine (red), ground (blue), and dissolving (CHCl_3)-drying (gray) samples for **3d**. The simulated single-crystal X-ray diffraction (SCXRD) pattern of **3d** was also included for comparison.

significant steric strain, which in turn would affect its absorption and/or emission properties. Thus, we investigated the mechanochromic behavior in a solid state. To elucidate the effect of *ortho* substituents, we examined N₂AQD derivatives **3a**, **3b**, and **3d**, which differ in the number of methyl groups at the *ortho* position on the 4-methoxyphenyl group. For derivatives **3a** with no *ortho* methyl group and **3b** with one *ortho* methyl group, a change in emission behavior from yellow ($\lambda_{\text{em}}/\text{nm} = 516$ for **3a** and 491 for **3b**) to orange (654 for **3a** and 633 for **3b**) was observed upon grinding the pristine crystals with a folded conformation (Figures S21–S22). The original crystals with yellow emission ($\lambda_{\text{em}}/\text{nm} = 540$ for **3a** and 500 for **3b**) were recovered by dissolving the ground powders in CHCl₃ and subsequent drying. Powder X-ray diffraction (PXRD) analyses revealed that this mechanochromic emission was based on a phase transition from crystal to amorphous. In addition, the color of the samples under daylight was also switched from yellow to orange by applying a mechanical stimulus. Thus, these N₂AQD derivatives have both ground-state and excited-state mechanochromic behaviors. Furthermore, more enhanced mechanochromic behavior was observed for **3d** with two *ortho* methyl groups. As shown in Figure 6, when yellow pristine crystals of **3d** with a folded conformation were ground in an agate mortar and pestle, the color of the crystals drastically changed from yellow to red, accompanied by a change in emission color from yellow to red. Diffuse reflectance and solid-state emission spectroscopies revealed significant shifts in absorption and emission maxima from 429 and 597 nm to 450 and 671 nm, respectively.

These spectral changes were fully reversible after the dissolving-drying process with CHCl₃. This dual-state mechanochromic response can be attributed to a conformational

change from a folded to a twisted geometry, triggered by the crystal-to-amorphous phase transition. Because *ortho*-dimethyl-substituted **3d** adopts the least folded conformation among a series of N₂AQD **3**, it is highly likely that the contribution of the twisted form significantly increased with the phase transition.

Finally, to explore the potential of N₂AQD **3** for multifunctional applications, we investigated its electrochromic behavior. Upon constant-current electrochemical oxidation of **3b** in CH₂Cl₂, the pale-yellow solution gradually turned blue, as monitored by UV–vis–NIR spectroscopy (Figure 7). This change with several isosbestic points at 372 and 327 nm indicates that the concentration of an intermediary radical cationic species is negligibly small, which is characteristic of *dyrex* systems. Due to the short-lived nature of the reactive open-shell intermediate, a reversible electrochromic response was clearly observed. Therefore, N₂AQD derivatives **3** exhibit three-way chromic responses: not only dual-state mechanochromism in the solid state, but also electrochromism in solution. These findings offer valuable design principles for the development of advanced chromic materials.

Conclusion

In this study, we developed a series of nitrogen-embedded anthraquinodimethanes (N₂AQDs) designed to exhibit multiple chromic behaviors through structural modification and steric control. By introducing *ortho*-substituted aryl groups onto a π -extended phenanthrene-fused backbone, we achieved a balance between conformational flexibility and rigidity, along with redox switchable property. Thus, the resulting N₂AQD derivatives **3a–3d** were found to undergo reversible conformational switching in the solid state and redox interconversion in solution. X-ray crystallographic and spectroscopic analyses revealed that the degree of *ortho* substituents can affect both the electronic properties and the conformational preference of the strained molecules. As a result, all N₂AQD derivatives exhibited solid-state mechanochromism, including both ground-state (color) and excited-state (emission) responses. Among them, *ortho*-dimethyl derivative **3d** showed the most prominent changes, due to increased steric strain. In addition, reversible electrochromic behavior was confirmed in solution through UV–vis–NIR spectroscopy. These findings clearly demonstrate that N₂AQDs are a promising platform for developing three-way chromic materials. Moreover, this study offers rational design principles for creating advanced organic systems that can respond to both mechanical and electrical stimuli.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for all compounds.

Synthetic details, characterization data, theoretical study and spectroscopic, and crystallographic details (PDF)

X-ray crystallographic data (CIF)

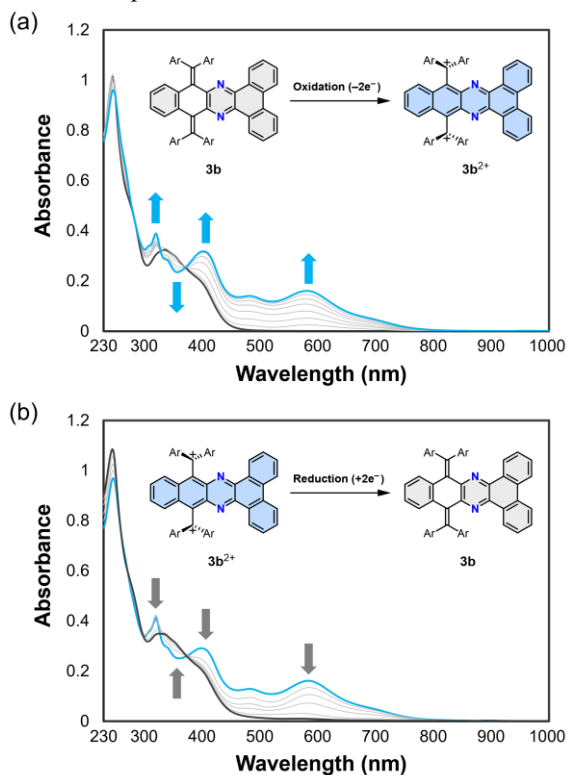


Figure 7. Changes in UV–vis–NIR spectra upon constant-current electrochemical (a) oxidation of **3b** (14.2 μM , 20 μA , every 8 min) and (b) subsequent reduction of as-prepared **3b²⁺** (20 μA , every 8 min) in CH₂Cl₂ containing 0.05 M Bu₄NBF₄ as the supporting electrolyte (**3b**/**3b²⁺**; Ar = 4-MeO-2-MeC₆H₃).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid from MEXT and JSPS (Nos. JP25K08604 to T.S. and JP23H04011, JP25H00873, JP25H01259, and JP25K22250 to Y.I.) and JST PRESTO (JPMJPR23Q1 to Y.I.). Y.I. and T.O. are grateful for the Toyota Riken Scholar Program. This work was also supported by the Research Program of “Five-star Alliance” in “NJRC Mater. & Dev.” MEXT.

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