

Three-way-output response system by electric potential: UV–vis, CD, and fluorescence spectral changes upon electrolysis of the chiral ester of tetracyanoanthraquinodimethane

Hiroki Higuchi,^a Koji Ichioka,^a Hidetoshi Kawai,^a Kenshu Fujiwara,^a Masakazu Ohkita,^b Takashi Tsuji^a and Takanori Suzuki^{a,*}

^aDivision of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

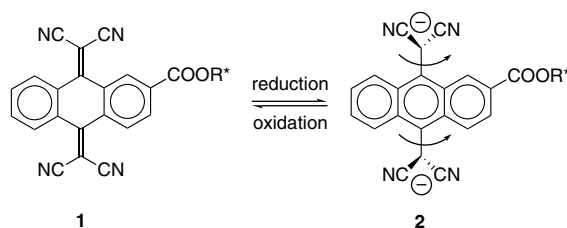
^bDepartment of Applied Chemistry, Faculty of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

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Abstract—The newly prepared tetracyanoanthraquinodimethane (TCNAQ) derivatives **1a,b** with a chiral auxiliary are good electron acceptors and exhibit weak circular dichroism (CD) based on the absorption of TCNAQ. The twin-type electron acceptor **1c** with two TCNAQ units shows larger ellipticity by exciton coupling. UV–vis, CD, and fluorescence spectra were changed drastically upon electrochemical reduction of **1c**, which demonstrates the unprecedented three-way-output response system.

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Electrochiroptical materials are the novel class of multi-output response systems, by which the electrochemical input is transduced into two kinds of spectral outputs, that is UV–vis and circular dichroism (CD). Compared with the extensive studies on the electrochromic material giving the UV–vis spectral change as a sole output,¹ there have been only a few successful examples of two-way-output redox systems reported so far.² Furthermore, there is no precedent that shows spectral outputs more than three kinds upon electrolysis. During the course of our continuing study on the electrochromic systems, we have found that the title electron acceptor **1** is a promising candidate as a novel three-way-output response system (Scheme 1). This material has been designed from the following viewpoints: (1) the tetracyanoanthraquinodimethane (TCNAQ) moiety will work as a strong chromophore, which induces UV–vis spectral change upon electrolysis,³ (2) the chiroptical output will be obtained when this chromophore is attached with an asymmetric element like a chiral ester group, (3) the nonfluorescent TCNAQ will become fluorescent upon reduction thanks to the anthracene skeleton produced in the anionic state. The last point



Scheme 1.

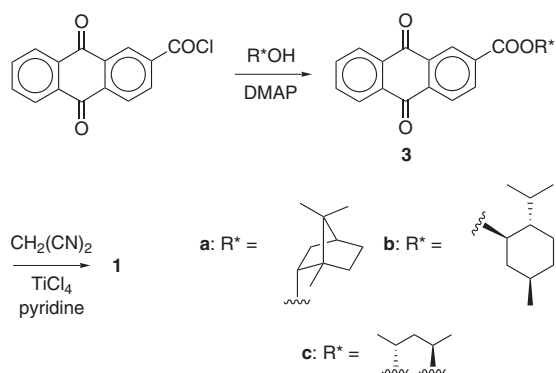
has never been considered before. Here we report a successful example of the unprecedented multi-output response system giving three-way spectral changes (UV–vis, CD, and fluorescence) upon electrolysis.

Reactions of anthraquinone-2-carbonyl chloride with (–)-borneol and (–)-menthol gave the chiral anthraquinone derivatives **3a,b**, which were then reacted with malononitrile⁴ to give the chiral TCNAQ derivatives **1a,b** in 69% and 62% yield, respectively, over two steps (Scheme 2).⁵ By starting with (2*R*, 4*R*)-(–)-pentane-2,4-diol, twin-type compound **1c** connected with the chiral spacer could be prepared in 87% yield via **3c**.

According to the voltammetric analysis, reduction potential of **1a** (E^{red} , –0.31 V vs SCE in CH₃CN) and **1b** (–0.32 V) are close to the 2e-reduction potential of the

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* Corresponding author. Tel.: +81-11-706-2714; fax: +81-11-706-2714; e-mail: tak@sci.hokudai.ac.jp



Scheme 2.

TCNAQ–methyl ester (**1d**, $R^*=Me$, -0.31 V),⁶ indicating that the reduction wave in **1a** or **1b** also corresponds to the reversible 2e-process. Neutral acceptors **1a,b** are light yellow and nonfluorescent. As shown in Figures 1 and 2, the electrochemical reduction of **1a,b** to **2a,b** caused a continuous UV–vis spectral changes, and vivid color change to violet corresponds to the growing new broad band in the visible region (λ_{max} 575 nm for **1a** and 576 nm for **1b**), which is characteristic to the TCNAQ dianion.³ The isosbestic points observed in the spectra are indicative of a clean transformation from **1a,b** to **2a,b** as well as of the negligible steady-state concentration of the intermediate anion radical. The latter comes from the dynamic redox properties of TCNAQ: much easier reduction of the twisted TCNAQ⁻ to the TCNAQ²⁻ than the TCNAQ to the butterfly-shaped

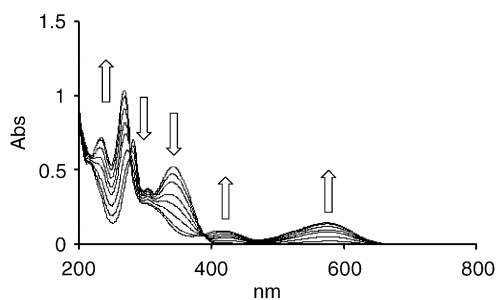


Figure 1. Changes in the UV–vis spectrum of **1a** (2.0×10^{-5} mol dm^{-3} in CH_3CN containing 0.05 mol dm^{-3} $n-Bu_4NBF_4$) upon constant-current electrochemical reduction ($29 \mu A$ at 4 min interval) to **2a**.

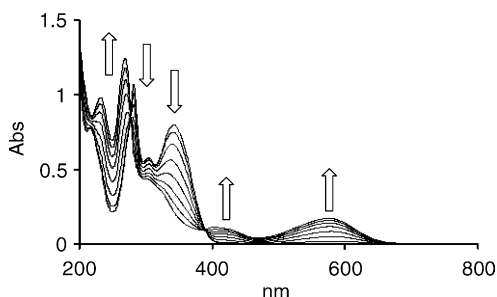


Figure 2. Changes in the UV–vis spectrum of **1b** (3.5×10^{-5} mol dm^{-3} in CH_3CN containing 0.05 mol dm^{-3} $n-Bu_4NBF_4$) upon constant-current electrochemical reduction ($29 \mu A$ at 4 min interval) to **2b**.

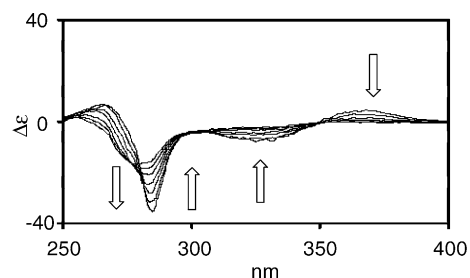


Figure 3. Changes in the CD spectrum of **1c** (4.4×10^{-5} mol dm^{-3} in CH_3CN containing 0.05 mol dm^{-3} $n-Bu_4NBF_4$) upon constant-current electrochemical reduction ($27 \mu A$ at 4 min interval) to **2c**.

TCNAQ⁻.^{3,4a,7} The one-wave 2e-reduction process of TCNAQ unit is favorable for constructing the reversible electrochromic systems because of the lack of destructive side reactions from the open-shell species.^{7,8} After the electrolysis, the solutions became fluorescent (λ_{em} 534 nm for **1a** and 533 nm for **1b** in CH_3CN). However, the CD signals of **1a,b** are too weak ($|\Delta\epsilon| \leq 1.5$) to be used as spectral outputs, so we finally gave up constructing the novel three-way-output response system by using **1a,b**.

On the contrary, the twin-type compound **1c** is much more CD active [$\lambda(\Delta\epsilon)$ 367 (+4.15), 324 (−5.61), 304 (−1.45), 285 (−28.1), 270 (+3.93), 229 (−7.14) nm in CH_3CN]. The couplet originated from characteristic TCNAQ absorption (300–400 nm) suggests exciton coupling between two chromophores.^{9,10} The through-space interaction between two TCNAQ units in **1c** is also evident from the less negative reduction potential (-0.23 V) than **1a,b**. Since only one pair of reduction waves were observed down to -2 V, **1c** may undergo one-wave 4e-reduction to the tetraanionic species **2c**. When the electrochemical study of **1c** was followed by CD spectroscopy, drastic change was observed as shown in Figure 3. Since the UV–vis spectrum is also changed upon electrolysis (Fig. 4), the redox pair of **1c** and **2c** can serve as a new entry of electrochiroptical system. Furthermore, upon electrochemical reduction of **1c**, fluorescence intensity increased gradually as shown in Figure 5. This is the first successful example by which the electrochemical input is transduced into three independent spectral outputs. Studies on other twin-type TCNAQs¹¹ are now under way.

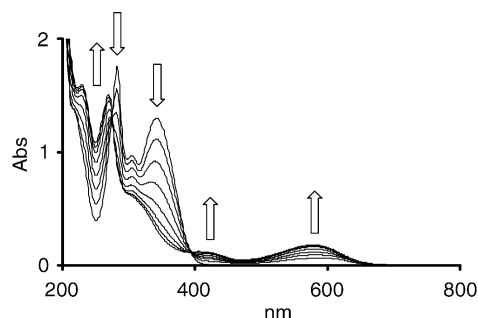


Figure 4. Changes in the UV–vis spectrum of **1c** (2.7×10^{-5} mol dm^{-3} in CH_3CN containing 0.05 mol dm^{-3} $n-Bu_4NBF_4$) upon constant-current electrochemical reduction ($29 \mu A$ at 4 min interval) to **2c**.

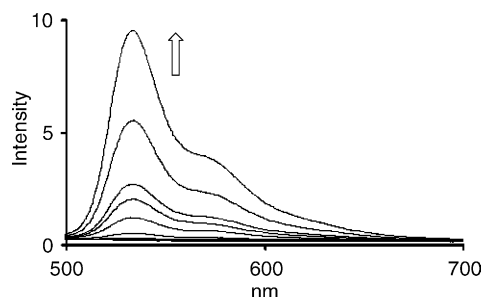


Figure 5. Changes in the fluorescence spectrum of **1c** ($2.7 \times 10^{-5} \text{ mol dm}^{-3}$ in CH_3CN containing 0.05 mol dm^{-3} $n\text{-Bu}_4\text{NBF}_4$) upon constant-current electrochemical reduction ($28 \mu\text{A}$ at 4 min interval) to **2c** ($\lambda_{\text{ex}} = 400 \text{ nm}$).

Acknowledgements

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- Selected data for new compounds are as follows: **1a** (y. 75%) light yellow powder, mp 290–291 °C dec, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.93 (1H, d, $J = 1.4$ Hz), 8.39 (1H, dd, $J = 8.0, 1.4$ Hz), 8.33 (1H, d, $J = 8.0$ Hz), 8.33–8.23 (2H, m), 7.82–7.73 (2H, m), 5.18 (1H, ddd, $J = 9.8, 3.4, 1.9$ Hz), 2.57–2.44 (1H, m), 2.21–2.09 (1H, m), 1.92–1.75 (2H, m), 1.63–1.25 (2H, m), 1.15 (1H, dd, $J = 14.0, 3.4$ Hz), 0.98 (3H, s), 0.94 (6H, s); IR (KBr) 2952, 2224, 1732, 1270, 1130, 774, 694 cm^{-1} ; MS (FD) m/z 484 (M^+ , BP); UV–vis (CH_3CN) λ_{max} 342 (log ϵ 4.41), 305 (4.26), 282 (4.53), 216 (4.40) nm; $[\alpha]_{\text{D}}^{24} -16.2$ (c 1.0, CHCl_3); CD (CH_3CN) λ 303 ($\Delta\epsilon +0.60$), 286 (+0.37), 278 (+0.77), 243 (–0.80), 230 (–0.22), 216 (–1.07) nm. **1b** (y. 70%) light yellow powder, mp 139–142 °C, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.90 (1H, d, $J = 1.4$ Hz), 8.38 (1H, dd, $J = 8.2, 1.4$ Hz), 8.32 (1H, d, $J = 8.2$ Hz), 8.32–8.22 (2H, m), 7.82–7.72 (2H, m), 4.99 (1H, td, $J = 10.9, 4.4$ Hz), 2.19–2.09 (1H, m), 2.02–1.89 (1H, m), 1.82–1.70 (2H, m), 1.67–1.47 (2H, m), 1.27–0.87 (3H, m), 0.94 (3H, d, $J = 6.8$ Hz), 0.93 (3H, d, $J = 6.8$ Hz), 0.78 (3H, d, $J = 6.9$ Hz); IR (KBr) 2952, 2224, 1732, 1552, 1270, 1130, 774, 694 cm^{-1} ; MS (FD) m/z 138 (BP), 486 (M^+ , 48%); UV–vis (CH_3CN) λ_{max} 342 (log ϵ 4.36), 305 (4.23), 282 (4.49), 216 (4.36) nm; $[\alpha]_{\text{D}}^{24} -38.7$ (c 1.0, CHCl_3); CD (CH_3CN) λ 351 ($\Delta\epsilon -0.37$), 303 (+1.51), 286 (+0.94), 280 (+1.18), 243 (–1.05), 229 (+0.23) nm. **1c** (y. 96%) light yellow powder, mp 195–208 °C dec, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.86 (2H, br), 8.35–8.16 (8H, br m), 7.82–7.73 (4H, br m), 5.50–5.32 (2H, br m), 2.22–2.10 (2H, br m), 1.44 (6H, br d, $J = 6.3$ Hz); IR (KBr) 2984, 2224, 1732, 1558, 1336, 1296, 1268, 1204, 1180, 1130, 1104, 774, 692 cm^{-1} ; MS (FD) m/z 382 (BP), 764 (M^+ , 75%); UV–vis (CH_3CN) λ_{max} 343 (log ϵ 4.68), 306 (4.55), 283 (4.81), 217 (4.67) nm; $[\alpha]_{\text{D}}^{22} -86.8$ (c 0.5, CHCl_3); CD see text. **3a** (y. 92%) light yellow needles, mp 167–168 °C, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.95 (1H, d, $J = 1.5$ Hz), 8.45 (1H, dd, $J = 8.3, 1.5$ Hz), 8.40 (1H, d, $J = 8.3$ Hz), 8.40–8.30 (2H, m), 7.90–7.81 (2H, m), 5.20 (1H, ddd, $J = 9.8, 3.5, 2.2$ Hz), 2.60–2.45 (1H, m), 2.25–2.12 (1H, m), 1.93–1.75 (2H, m), 1.55–1.32 (2H, m), 1.18 (1H, dd, $J = 13.8, 3.5$ Hz), 0.93 (3H, s), 0.95 (3H, s), 0.94 (3H, s); IR (KBr) 2952, 1724, 1682, 1594, 1334, 1272, 1248, 702 cm^{-1} ; MS (FD) m/z 388 (M^+ , BP); UV–vis (CH_3CN) λ_{max} 325 (log ϵ 3.68), 271 (sh, 4.22), 256 (4.73), 212 (4.52) nm; $[\alpha]_{\text{D}}^{25} -24.4$ (c 1.0, CHCl_3); CD (CH_3CN) λ 280 ($\Delta\epsilon +0.50$), 271 (+0.89), 253 (+2.41), 239 (+1.82), 212 (+5.49) nm. **3b** (y. 89%) light yellow powder, mp 71–73 °C, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.93 (1H, d, $J = 1.6$ Hz), 8.44 (1H, dd, $J = 8.3, 1.6$ Hz), 8.39 (1H, d, $J = 8.3$ Hz), 8.39–8.29 (2H, m), 7.83–7.80 (2H, m), 5.02 (1H, td, $J = 10.9, 4.4$ Hz), 2.19–2.10 (1H, m), 1.96 (1H, septet d, $J = 7.0, 2.6$ Hz), 1.82–1.71 (2H, m), 1.69–1.51 (2H, m), 1.26–0.89 (3H, m), 0.95 (3H, d, $J = 6.8$ Hz), 0.94 (3H, d, $J = 6.8$ Hz), 0.81 (3H, d, $J = 6.9$ Hz); IR (KBr) 2952, 1722, 1680, 1272, 1246, 706 cm^{-1} ; MS (FD) m/z 138 (BP), 388 ($\text{M}^+ -2$, 68%), 389 ($\text{M}^+ -1$, 38%), 390 (M^+ , 25%); UV–vis (CH_3CN) λ_{max} 325 (log ϵ 3.70), 270 (sh, 4.25), 256 (4.75), 212 (4.55) nm; $[\alpha]_{\text{D}}^{23} -68.9$ (c 1.0, CHCl_3); CD (CH_3CN) λ 254 ($\Delta\epsilon +1.45$), 230 (–0.52), 214 (+0.81) nm. **3c** (y. 91%) light yellow powder, mp 192–193 °C, ^1H NMR (300 MHz, CDCl_3) δ /ppm 8.73 (2H, dd, $J = 1.5, 0.6$ Hz), 8.32 (2H, ddd, $J = 8.1, 1.5, 0.6$ Hz), 8.23 (2H, d, $J = 8.1$ Hz), 8.27–8.15 (4H, m), 7.81–7.72 (4H, m), 5.47 (2H, sextet, $J = 6.3$ Hz), 2.23 (2H, t, $J = 6.3$ Hz), 1.48 (6H, d, $J = 6.3$ Hz); IR (KBr) 2984, 1722, 1680, 1594, 1330, 1296, 1274, 1246, 1170, 1140, 1112, 1084, 932, 798, 706 cm^{-1} ; MS (FD) m/z 572 (M^+ , BP); UV–vis (CH_3CN) λ_{max} 327 (log ϵ 4.03), 272 (sh, 4.49), 254 (4.96), 212 (4.87) nm; $[\alpha]_{\text{D}}^{23} -199$ (c 0.5, CHCl_3); CD (CH_3CN) λ 334 ($\Delta\epsilon -5.14$), 299 (–1.73), 261 (–57.8), 248 (+46.2), 223 (–0.07), 210 (+32.6) nm.
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10. Preparation of twin-type TCNAQs connected by the chiral binaphthyl-6,6'-diyl spacer was reported previously, but the intramolecular interaction between two TCNAQ units was shown to be negligible. No chiroptical properties (CD, $[\alpha]$) of them were reported: Gómez, R.; Segura, J. L.; Martín, N. *J. Org. Chem.* **2000**, *65*, 7566–7574.
11. Preliminary study shows that the twin-type TCNAQ containing the chiral binaphthyl-2,2'-diyl moiety could be prepared from (*R*)-2,2'-binaphthol, but it did not show the clean spectroelectrogram like Figure 4 probably due to adsorption of the anionic species on the electrode or due to some side reaction upon reduction.