HETEROCYCLES, Vol. 95, No. 2, 2017, pp. 816-829. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 29th August, 2016, Accepted, 24th October, 2016, Published online, 31st January, 2017
DOI: 10.3987/COM-16-S(S)50

OXIDATIVE DESULFURIZATION OF ELECTRON-DONATING 5,5,7,7-TETRAARYL-5,7-DIHYDRODIBENZO[*c,e*]THIEPINS AND THE RELATED HETEROCYCLES: GENERATION OF DICATIONIC DYES UPON TWO-ELECTRON OXIDATION

Takanori Suzuki,* Takuma Kuroda, Hitomi Tamaoki, Sho Higasa,[†] Tatsuo Nehira,[††] Ryo Katoono, Yusuke Ishigaki, Kenshu Fujiwara,[†††] Takanori Fukushima,[††††] and Hidetoshi Yamada[†]

Dedicated to Prof. Dr. Masakatsu Shibasaki on the occasion of his 70th birthday

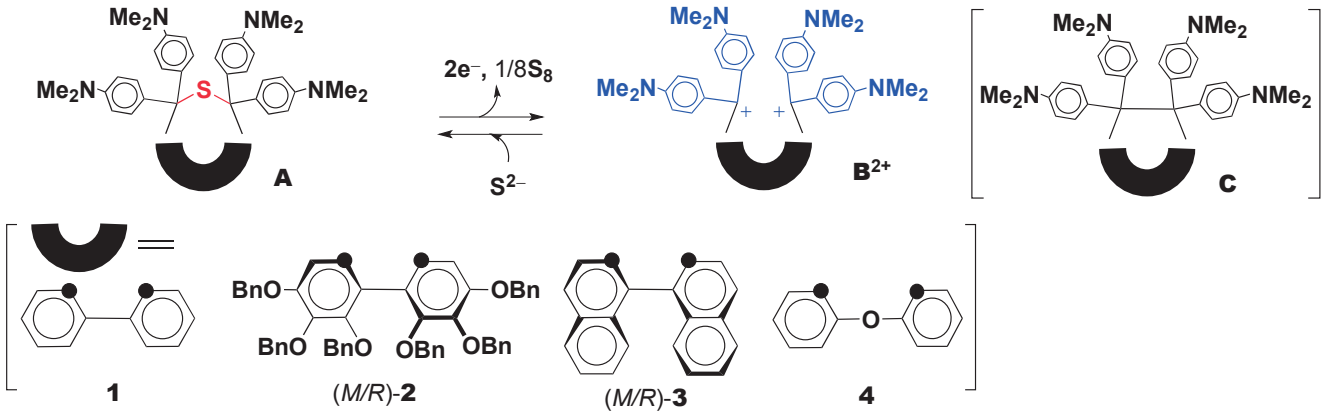
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. [†]School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan. [††]Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8521, Japan. [†††]Graduate School of Engineering Science, Akita University, Akita 010-8502, Japan. [††††]Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan

Abstract – Upon oxidation of the title heterocycle (**1A**) with dimethylamino groups, elemental sulfur is extruded to form dicationic dye (**1B**$^{2+}$), from which the starting dibenzothiepin derivative was generated by the reaction with Na_2S. The bay-region substituents enhance configurational stability, so that, the optically pure heterocycles [(*M*)-**2A**, (*M*)-**3A**)] can be obtained in terms of helicity of one-handedness by starting with the corresponding optically pure dicationic dyes [(*R*)-**2B**$^{2+}$, (*R*)-**3B**$^{2+}$)]. Similar oxidative desulfurization occurs in dibenzo-1,5-oxathiocin **4A**, a structurally related 8-membered heterocycle.

INTRODUCTION

5,7-Dihydrodibenzo[*c,e*]thiepin (DHDBT) is a less well-explored heterocycle, yet its potent biological acitivity has attracting some attention.[1,2] As found in many organosulfur compounds exhibiting unique reactivities which are absent in the oxygen congeners, redox activation of sulfur would enable various

transformations, thus adding useful knowledge for the development of sulfur-based organic synthesis[3] and materials chemistry.[4] Oxidation of sulfides commonly induces oxygenation on sulfur to give the corresponding sulfoxides and sulfones.[5] This is also the case of DHDBT with no substituents at 5,7-positions.[2] On the other hand, we have recently found that a facile C-S bond mesolysis[6] was induced upon oxidation of DHDBT derivatives (**1A**[7] and **2A**) with four electron-donating aryl groups at 5,7-positions[8] (Scheme 1). Although desulfurization accompanied by C–S bond fission occurs under electron-transfer conditions as reported for strained thiiranes[9] or aryl benzyl sulfides,[10] the above mentioned reaction of tetraaryl-DHDBT is intriguing in the sense that the stable dicationic dyes (**1B**$^{2+}$ and **2B**$^{2+}$) were generated, from which heterocycles **1A** and **2A** are obtained by the reaction of Na_2S. Here we report the details on the novel desulfurization of tetraaryl-DHDBTs (**1A** and **2A**)[8] along with the X-ray structures and the reactivities of the related heterocycles (**3A** and **4A**), which were newly prepared from **3B**$^{2+}$ and **4B**$^{2+}$, respectively.



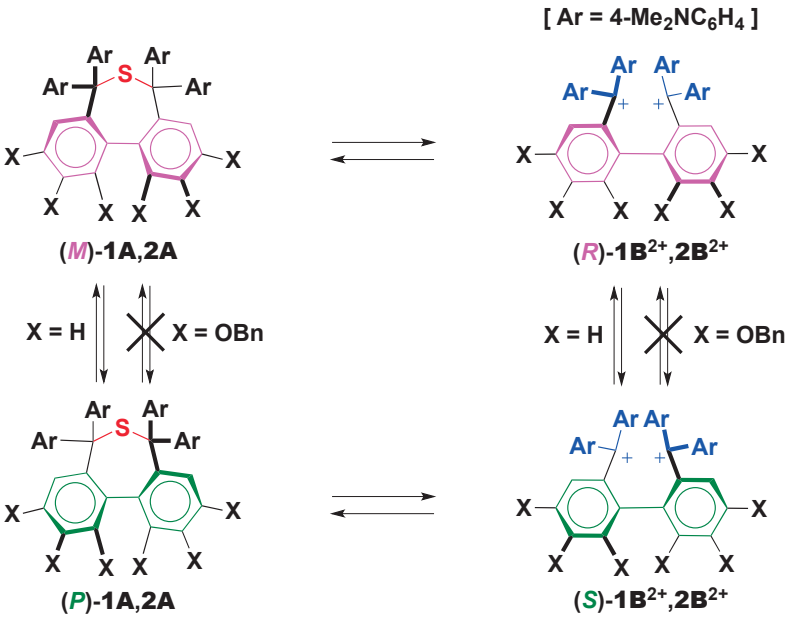
Scheme 1. Oxidative desulfurization of heterocycles **1A** - **4A** into dications **1B**$^{2+}$ - **4B**$^{2+}$

RESULTS AND DISCUSSION

Preparation and Molecular Structures of Tetraaryl-DHDBTs and the Related Heterocycles

Biphenyl-2,2'-diylbis[bis(4-dimethylaminophenyl)carbenium **1B**$^{2+}$ is a persistent dicationic dye[11] with two units of malachite green (MG^+) chromophores. The well-split absorptions in the visible region [λ_{max} / nm (ε) in CH_2Cl_2: 662 (69100), 611 (87500)] result from Davydov splitting of the x-band[12] of MG^+ [623 (102000)], showing strong intramolecular interaction between two chromophores. Upon electrochemical reduction of **1B**$^{2+}(BF_4^-)_2$, a new C–C bond is formed between the two methylium carbons to give dihydrophenanthrene derivative **1C**,[11,13] which was also formed by treating **1B**$^{2+}(BF_4^-)_2$ with Zn dust. In contrast, we have recently found that, upon treatment of **1B**$^{2+}(BF_4^-)_2$ with Na_2S, not reduction product **1C** but 7-membered sulfur heterocycle **1A** was formed as the first member of tetraaryl-DHDBT.[7] The quantitative yield of **1A** from **1B**$^{2+}(BF_4^-)_2$ is outstanding since **1A** would suffer from steric

congestion[14] around the suflur atom by the two triarylmethyl units. In fact, the DFT calculation (B3LYP/6-31G(d)) as well as the X-ray analysis indicated that **1A** adopts a skewed conformation to minimize steric hindrance (Figure 1a).[7] The biphenyl skeleton in **1A** is twisted (torsion angle: 53.2°), as in the case of $\mathbf{1B}^{2+}$ in $(SbCl_6^-)_2$ salt (X-ray: 69°).[11] Thus, both **1A** and $\mathbf{1B}^{2+}$ are endowed with a chiral element of helicity and axial chirality, respectively, although interconversion between enantiomers proceeds at room temperature[7] (Scheme 2).



Scheme 2. Different configurational stability by bay-region substituents

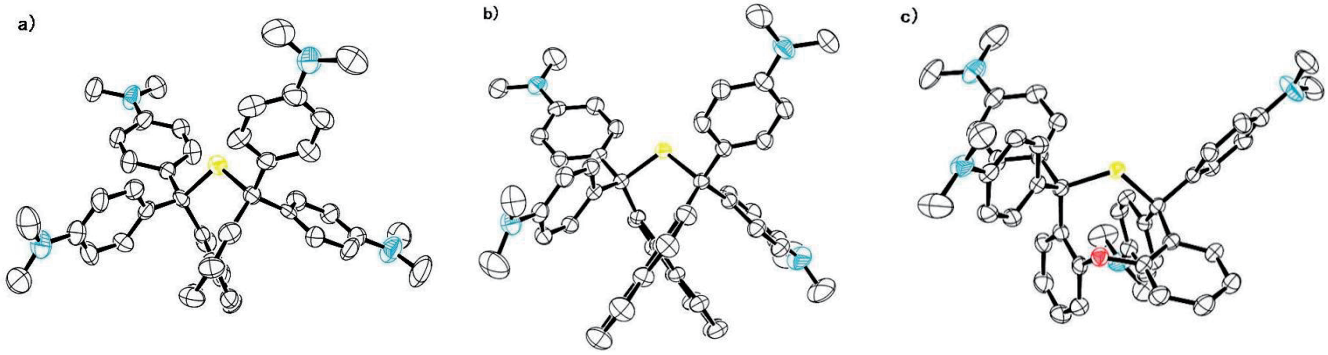
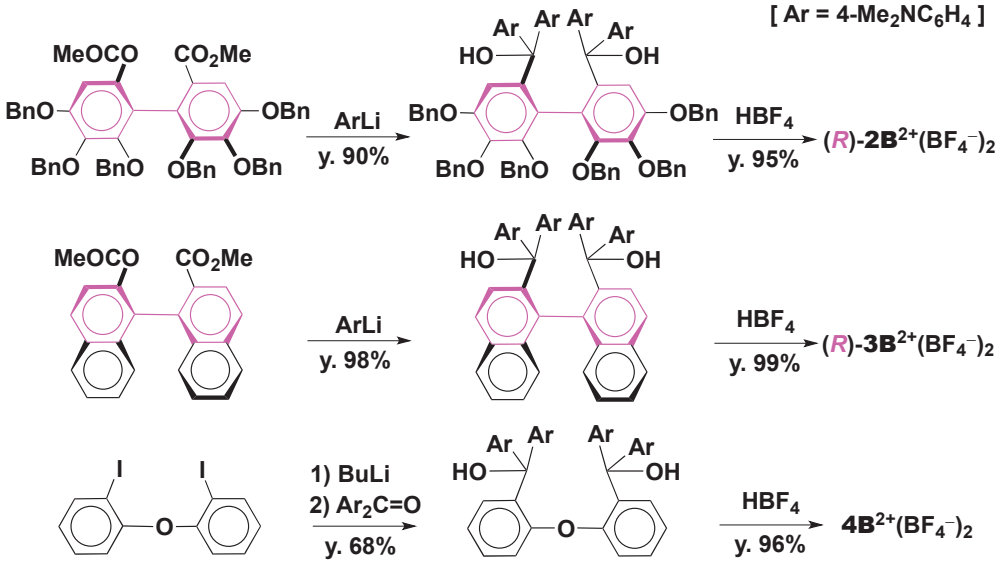


Figure 1. ORTEP drawings of a) **1A**, b) **3A**, and c) **4A** determined by X-ray structural analyses

Introduction of bulky bay-region substituents would increase configurational stability by raising the racemization barrier of DHDBT. For this purpose, $\mathbf{2A}$[8] and **3A** were desinged, which are attached with six benzyloxy groups or dibenzo annulation, respectively. Their dicationic precursors were obtained by the reactions of the corresponding axially chiral diesters[15,16] as shown in Scheme 3. The *M* enantiomer of **2A** was obtained in 90% yield upon Na_2S-treatment of (*R*)-$\mathbf{2B}^{2+}(BF_4^-)_2$.[8] Both redox states of these hexabenzyloxy derivatives are configurationally stable and exhibit large Cotton effects in their CD spectra (Figures S1 and S2). There were no signs of racemization upon transformation or standing. Similarly, configurationally stable 3,5-dihydro-3,3,5,5-tetraaryldinaphtho[2,1-*c*:1',2-*e*]thiepin (*M*)-**3A** was obtained from 1,1'-binaphthyl-2,2'-diylbis(diarylmethylium) (*R*)-$\mathbf{3B}^{2+}(BF_4^-)_2$ in 68% yield. This pair

also exhibits very strong CD signals (Figure S2), which did not show any decay upon standing. According to the X-ray analysis,[17] dinaphthothiepin **3A** adopts a more skewed geometry with a torsion angle of 69.4º for the binaphthyl group (Figure 1b), thus demonstrating the steric bulkiness by dibenzo annulation that increases the racemization barrier.

To explore the scope and limitations, 8-membered ring analogue **4A** was also designed and obtained in 73% yield upon Na_2S-treatment of **4B**$^{2+}(BF_4^-)_2$, which in turn was prepared from 2,2'-diiododiphenyl ether (Scheme 3). The 5,7-dihydrodibenzo[*b*,*g*][1,5]oxathiocin skeleton has been only scarcely studied,[18] yet the structural identity of **4A** was unambiguously determined by X-ray analysis. As shown in Figure 1c, the 8-membered ring in **4A** adopts a tub form in its hexane solvated crystal. Based on the ^{1}H NMR spectrum ($CDCl_3$, 25 ºC), **4A** has a higher conformational flexibility. Thus, the four aryl groups appeared as a single set of resonances, which is in sharp contrast to those for other heterocycles **1A** - **3A** exhibiting two sets of signals assigned to the aryl groups at the pseudo-axial and pesudo-equatorial positions, respectively, in the skewed conformation of the 7-membered ring.



Scheme 3. Preparation of dication salts **2B**$^{2+}(BF_4^-)_2$ - **4B**$^{2+}(BF_4^-)_2$

Oxidative Desulfurization of Tetraaryl-DHDBTs and the Related Heterocycles

According to the voltammetric analyses (Figure S3), heterocycles **1A** - **4A** are strong electron donors. They undergo electrochemical oxidation at $E_{1/2}$ = +0.57, +0.59, +0.55, and +0.47 V vs SCE, respectively. These oxidation potentials are close to that of dibenzo-TTF (+0.57 V) measured under the similar conditions. All of the waves in the voltammograms of **1A** - **4A** are irreversible, suggesting that facile follow-up reactions (e.g. C–S mesolysis) occur upon oxidation. In fact, upon treatment of **1A** with 3 equiv. of iodine in CH_2Cl_2, a dark purple powder of **1B**$^{2+}(I_3^-)_2$ was obtained in 88% yield. From the filtrate, elemental sulfur was isolated in 31% yield. On the other hand, the higher steric restriction of the 7-membered ring is not a prerequisite for the ring-opening C–S mesolysis since the reaction of 8-membered-ring heterocycle **4A** proceeded smoothly to give **4B**$^{2+}(I_3^-)_2$ in 92% yield.

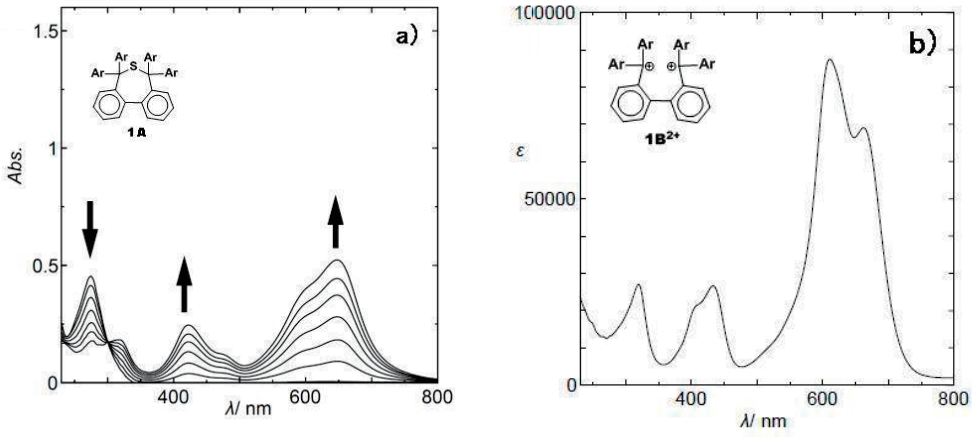


Figure 2. a) A continuous change in UV-Vis spectrum upon constant current electrochemical oxidation of **1A** (7.8×10^{-6} M) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 (5 micro A, every 4 min). b) UV-Vis spectrum of $\mathbf{1B}^{2+}(BF_4^-)_2$ in CH_2Cl_2.

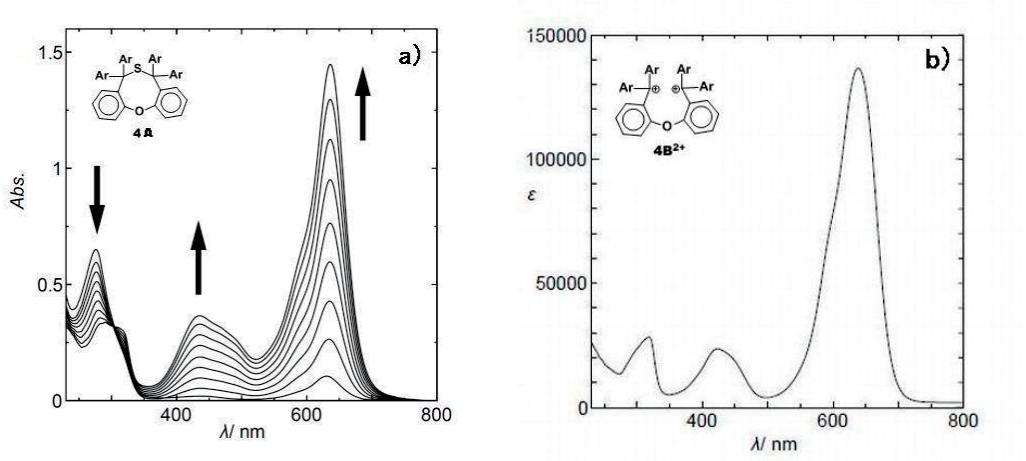
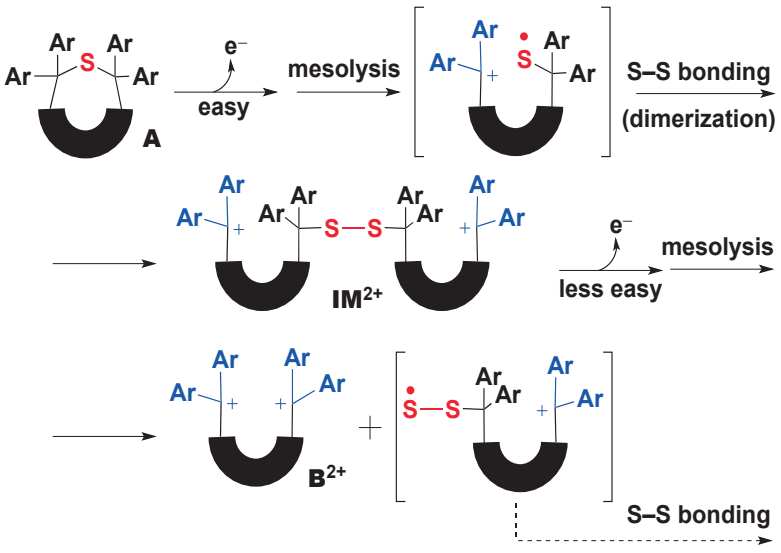


Figure 3. a) A continuous change in UV-Vis spectrum upon constant current electrochemical oxidation of **4A** (9.1×10^{-6} M) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 (5 micro A, every 4 min). b) UV-Vis spectrum of $\mathbf{4B}^{2+}(BF_4^-)_2$ in CH_2Cl_2.

When an electrolysis of tetraaryl-DHDBT **1A** was conducted in CH_2Cl_2, a deep blue color developed, which is characteristic to MG^+-type chromophore. A continuous change exhibiting several isosbestic points was observed by UV-Vis spectroscopy (Figure 2), demonstrating that the oxidation reaction of **1A** is accompanied by a chromic response[19] with a vivid change in color from colorless to deep



Scheme 4. Plausible mechanism for conversion of heterocycles **A** to dications $\mathbf{B}^{2+}$

blue. The newly appeared absorptions are not identical to those of dication $\mathbf{1B}^{2+}$ since the C–S mesolysis of **1A** would not directly give $\mathbf{1B}^{2+}$ but some cationic intermediates containing the MG^{+} chromophore (Scheme 4). Especially, dicationic intermediate $\mathbf{1IM}^{2+}$ would be long-lived since its further oxidation to cleave another C–S bond must be less easy than **1A** because of the presence of positive charges within the molecule. This holds also true for dibenzoxathiocin **4A** although the spectrum of the oxidized species closely resembles that of $\mathbf{1B}^{2+}$ (Figure 3).

Considering that the twisted π-systems exhibit strong circular dichroism (CD) signals by exciton coupling mechanism,[20] it is expected that the electrochemical oxidations of (*M*)-**2A** [λ_{ext} / nm ($\Delta\varepsilon$) in CH_2Cl_2: 243 (–67.6), 265 (+54.8), 306 (+30.3)] and (*M*)-**3A** [242 (–228), 281 (+37.2), 312 (+43.1)] would exhibit a large change in the CD spectrum. In fact, clean conversion exhibiting isosbestic points was observed not only in the UV-Vis but also in the CD spectra (Figures 4 and 5). Again, the resulting spectra upon oxidation are not identical to those of (*R*)-$\mathbf{3B}^{2+}$ or (*R*)-$\mathbf{4B}^{2+}$ (Figures S1 and S2), confirming that the formation of dications $\mathbf{B}^{2+}$ from sulfur heterocycles **A** composed of multi-step processes.[21]

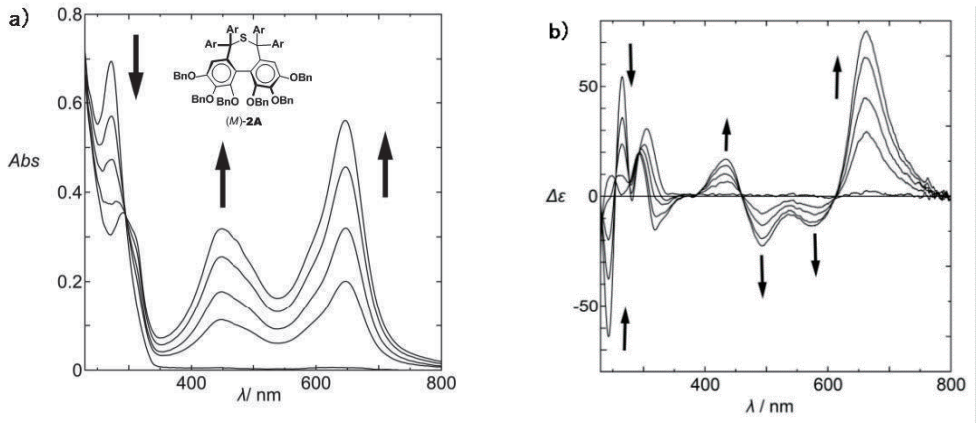


Figure 4. Continuous changes in a) UV-Vis and b) CD spectra upon constant current electrochemical oxidation of (*M*)-**2A** (9.1×10^{-6} M) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 (5 micro A, every 8 min).

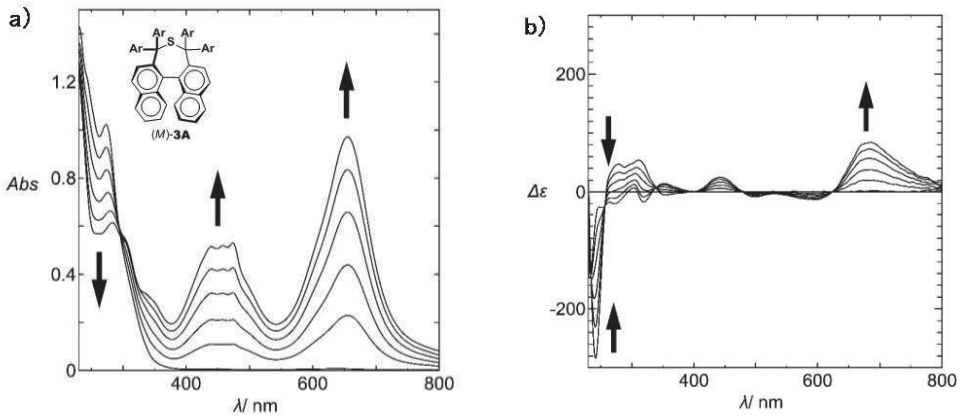
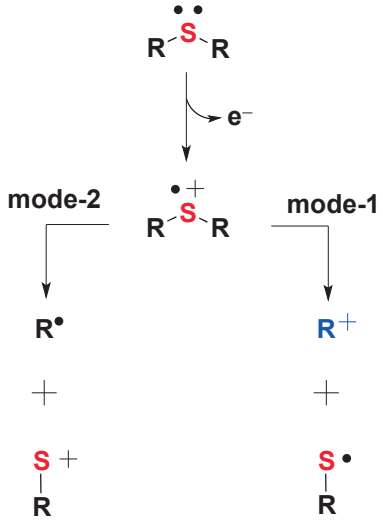


Figure 5. Continuous changes in a) UV-Vis and b) CD spectra upon constant current electrochemical oxidation of (*M*)-**3A** (1.3×10^{-5} M) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 (5 micro A, every 12 min).

SUMMARY

This paper describes the details on the novel oxidative transformation of DHDBTs and the related heterocycles into the corresponding dicationic dyes accompanied by extrusion of elemental sulfur. All of the heterocycles have the subunit of bis[bis(4-dimethylaminophenyl)phenylmethyl]sulfide ($PhAr_2C$-S-CAr_2Ph),[8] which is the core unit for this reaction to occur. As shown in Scheme 5, there would be two modes[22] for the mesolysis of sulfides (R–S–R) after one-electron oxidation. The mode-1 leads formation of carbocation (R^+) and thiyl radical ($^\bullet$S–R) whereas the mode-2 gives carbon radical (R$^\bullet$) and thiylium ($^+$S–R). Formation of thiyliums (mode-2) often occurs under the mass spectroscopy conditions.[23] Very high thermodynamic stability of MG^+ (pK_{R+}: 6.90)[24] is the key to switch the reaction pathway from mode-2 to mode-1 in the cation radicals of heterocycles **1A - 4A**. Thus, the similar oxidative desulfurization would be realized in other electron-donating sulfides when designed to incorporate the R moiety to be liberated as a thermodynamically stable carbocation (R^+).



Scheme 5. Two modes of mesolysis for sulfide cation radicals

EXPERIMENTAL

General. ^{1}H NMR spectra were recorded on a JEOL AL-300 (300 MHz). The chemical shifts are quoted relative to TMS in $CDCl_3$ unless indicated otherwise. IR spectra were taken on JEOL JIR-WINSPEC100 FT/IR spectrophotometer. Melting points were measured on Yamato MP-21 or Yanagimoto micro melting point apparatus and reported uncorrected. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer. CD spectra were measured on a JASCO J-820 spectropolarimeter. Mass spectra were recorded on a JMS-AX500, JMS-SX102A, or JEOL JMS-T100GCV spectrometers in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Elemental analyses were taken on a J-Science micro corder JM10 or Yanaco CHN corder MT-6 at the center for Instrumental Analysis of Hokkaido University.

Preparation of 5,7-dihydro-5,5,7,7-tetrakis(4-dimethylaminophenyl)dibenzo[*c*,*e*]thiepin (1A). To a solution of $Na_2S{\cdot}9H_2O$ (1.48 g, 6.16 mmol) in MeCN/H_2O (2:1 v/v) (60 mL) was added a solution of **1B**$^{2+}$(BF_4^-)$_2$[11] (1.02 g, 1.23 mol) in MeCN (50 mL) dropwise over 3.5 h at room temperature. Then, the mixture was stirred for 30 min. The resulting suspension was diluted with saturated aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and

brine. After drying over Na_2SO_4, the solvent was removed to give **1A** (905 mg, 100%) as a colorless solid. The analytical sample was obtained by recrystallization from AcOEt.

Data of **1A**: Decomp. 228-235 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.30-7.05 (br, 6H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.88 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 2H), 6.81 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 2H), 6.61 (br. d, *J* = 8.8 Hz, 4H), 6.46 (br. d, *J* = 8.8 Hz, 2H), 6.39 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.35 (br. s, 2H), 2.90 (s, 12H), 2.83 (s, 12H) ppm; IR (KBr) 3037, 2880, 2794, 1608, 1559, 1513, 1474, 1439, 1352, 1208, 1183, 1160, 1142, 1058, 1004, 948, 895, 811, 776, 749, 714, 578, 567, 535 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / $M^{-1}cm^{-1}$) 274 (60200); LR-MS (FD) *m/z* = 690 (20), 689 (55), 688 (M^+, bp); Anal. Calcd for $C_{46}H_{48}N_4S\cdot0.5C_4H_8O_2$: C 78.65, H 7.15, N 7.64. Found: C 78.67, H 7.85, N 7.50.

Preparation of (*M*)-5,7-dihydro-1,2,3,9,10,11-hexakis(benzyloxy)-5,5,7,7-tetrakis(4-dimethylamino-phenyl)dibenzo[*c,e*]thiepin [(*M*)-2A]. To a solution of (*R*)-**2B**$^{2+}$(BF_4^-)$_2$ (39.1 mg, 26.6 μmol) in MeCN (10 mL) was added aqueous $Na_2S\cdot9H_2O$ (335 mg, 1.37 mmol) (2 mL). The mixture was stirred for 2 h. The resulting suspension was extracted with AcOEt, and the combined organic layer was washed with water and brine. After drying over Na_2SO_4, the solvent was removed, and the residue was purified by flash chromatography (Al_2O_3, Et_2O:hexane = 1:2) to give (*M*)-**2A** (31.9 mg, 90%) as a greenish amorphous solid.

Data of (*M*)-**2A**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.37 (m, 12H), 7.15-7.34 (m, 18H), 6.85 (d, *J* = 7.2 Hz, 4H), 6.71 (s, 2H), 6.69 (m, 2H), 6.50 (m, 6H), 6.14 (dd, *J* = 8.8, 2.4 Hz, 2H), 5.03 (d, *J* = 12.6 Hz, 2H), 4.96 (d, *J* = 12.6 Hz, 2H), 4.95 (d, *J* = 13.0 Hz, 2H), 4.67 (d, *J* = 13.0 Hz, 2H), 4.31 (br. s, 4H), 2.88 (s, 12H), 2.74 (s, 12H); IR (KBr) 3061, 3029, 2878, 2796, 1607, 1514, 1496, 1479, 1452, 1422, 1359, 1317, 1210, 1163, 1100, 1027, 947, 815, 732, 696 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 272 (71500); CD (CH_2Cl_2): λ_{ext} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 243 (-67.6), 265 (+54.8), 306 (+30.3); LR-MS (FD) *m/z* = 1328 (23), 1327 (55), 1326 (99), 1325 (M^+, bp); HR-MS (FD) calcd. for $C_{88}H_{84}N_4O_6S$: 1324.6112; found: 1324.6083.

Preparation of *(R)*-4,4',5,5',6,6'-hexakis(benzyloxy)biphenyl-2,2'-bis[bis(4-dimethylamino-phenyl)methylium] bis(tetrafluoroborate) [(*R*)-2B^{2+}(BF_4^-)$_2$]. To a solution of 4-bromo-*N,N*-dimethylaniline (264 mg, 1.32 mmol) in THF (4 f) was added dropwise *n*-BuLi (1.64 M hexane solution, 0.80 mL, 1.38 mmol) at –78 °C. The mixture was stirred for 1 h at –78 °C, and then (*R*)-dimethyl 4,4',5,5',6,6'-hexakis(benzyloxy)biphenyl-2,2'-carboxylate[15] (118 mg, 130 μmol) was added as a solid. The mixture was warmed to room temperature and stirred for 15 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with AcOEt. The combined organic layer was washed with water and brine. After drying over Na_2SO_4, the solvent was removed to give a brown oil,

which was triturated with hexane. The resulting suspension was filtered to give diol (155 mg, 90%) as a bluish powder.

To a solution of diol (82.7 mg, 0.062 mmol) in THF (2.5 mL) was added a solution of 42% aqueous HBF_4 (0.025 mL, 0.16 mmol) in THF (2.5 mL), and the mixture was stirred for 21 h at room temperature. After diluted with Et_2O, the resulting suspension was filtered to give (*R*)-**3b**$^{2+}$(BF_4^-)$_2$ (85.7 mg, 94%) as a dark black powder.

Data of (*R*)-**3b**$^{2+}$(BF_4^-)$_2$: ^{1}H NMR (300 MHz, CD_3CN) δ 7.4-6.3 (br. m, 46H), 6.48 (s, 2H), 5.22 (d, *J* = 12.0 Hz, 2H), 5.13 (d, *J* = 12.0 Hz, 2H), 4.99 (d, *J* = 12.0 Hz, 2H), 4.96 (d, *J* = 12.0 Hz, 2H), 4.56 (d, *J* = 12.0 Hz, 2H), 4.46 (d, *J* = 12.0 Hz, 2H), 3.26 (s, 12H), 2.98 (s, 12H) ppm; IR (KBr) 1619, 1583, 1478, 1453, 1402, 1365, 1170, 1083, 939, 912, 733 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 314 (27900), 448 (26800), 616 (74500), 662 (62600); CD (CH_2Cl_2): λ_{ext} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 298 (+33.2), 318 (-37.3), 425 (+20.8), 606 (-190), 668 (+267); LR-MS (ESI) = 1383 (11), 1382 (34), 1381 (74), 1380 (M$^+$, 84), 1191 (10), 1190 (37), 1189 (bp); HR-MS (ESI) calcd. for $C_{88}H_{84}BF_4N_4O_6^+$: 1378.6451; found: 1378.6455

Preparation of (*M*)-3,5-dihydro-3,3,5,5-tetrakis(4-dimethylaminophenyl)dinaphtho[2,1-*c*:1',2'-*e*]thiepin [(*M*)-3A]. To a solution of **3B**$^{2+}$(BF_4^-)$_2$ (58.5 mg, 63 μmol) in MeCN/MeOH (3/2) (25 mL) was added aqueous $Na_2S\cdot 9H_2O$ (752 mg, 3.13 mol) (5 mL). The mixture was stirred for 13 h at room temperature. The resulting suspension was diluted with saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The combined organic layer was washed with water and brine. After drying over Na_2SO_4, the solvent was removed to give a green solid, which was purified by preparative TLC (SiO_2, AcOEt:hexane = 1:2) to give (*M*)-**3A** (16 mg) as a greenish amorphous solid in 32% yield.

Data of (*M*)-**3A**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8, 2H), 7.54 (m, 6H), 7.2-7.4 (m, 4H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.78 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 4H), 6.51 (d, *J* = 8.4 Hz, 4H), 6.14 (d, *J* = 8.8 Hz, 2H), 5.80 (d, *J* = 8.8 Hz, 2H), 2.82 (s, 12H), 2.52 (s, 12H) ppm; IR (KBr) 2922, 2879, 2847, 2792, 1608, 1513, 1479, 1442, 1347, 1209, 1184, 1159, 1129, 1058, 947, 817, 797, 752, 746, 566 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 273 (64200); CD (CH_2Cl_2): λ_{max} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 242 (-228), 281 (+37.2), 312 (+43.1); LR-MS (FD) *m/z* = 790 (26), 789 (69), 788 (M$^+$, bp); HR-MS (FD) calcd. for $C_{54}H_{52}N_4S$: 788.3913; found: 788.3890.

Preparation of *(R)* 1,1'-binaphthyl-2,2'-bis[bis(4-dimethylaminophenyl)methylium] bis(tetrafluoroborate) [(*R*)-3B^{2+}(BF_4^-)$_2$]. To a solution of 4-bromo-*N,N*-dimethylaniline (1.41 g, 7.04 mmol) in THF (10 mL) was added dropwise *n*-BuLi (1.65 M hexane solution, 4.0 mL, 6.60 mmol) at –78 °C. The mixture was stirred for 1 h at –78 °C, and then (*R*)-dimethyl 1,1'-binaphthyl-2,2'-

dicarboxylate[16] (402 mg, 1.09 mmol) was added as a solid. The mixture was warmed to room temperature and stirred for 16 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with AcOEt. The combined organic layer was washed with brine. After drying over Na_2SO_4, the solvent was removed to give a brown oil, which was triturated with hexane. The resulting suspension was filtered to give diol (832 mg, 97%) as a white powder.

To a solution of diol (180 mg, 0.23 mmol) in THF (11 mL) was added a solution of 42% aqueous HBF_4 (0.09 mL, 0.63 mmol) in THF (1.0 mL). After stirring for 46 h at room temperature, the mixture was diluted with Et_2O. The resulting suspension was filtered to give (*R*)-**3B**$^{2+}$(BF_4^-)$_2$ (187 mg, 88%) as a dark green powder.

Data of (*R*)-**3B**$^{2+}$(BF_4^-)$_2$: Decomp. 298-300 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.53 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.26-7.37 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.88-6.95 (m, 6H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 9.0 Hz, 4H), 3.25 (s, 12 H), 2.93 (s, 12H) ppm; IR (KBr) 1618, 1582, 1483, 1361, 1171, 1124, 1083, 1056, 939, 912, 836, 731 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 264 (20000), 306 (18300), 351 (12600), 422 (19300), 473 (18100), 638 (47900), 676 (40600); CD (CH_2Cl_2): λ_{max} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 235 (-84.3), 301 (+23.2), 322 (-32.4), 422 (+18.3), 622 (-107), 687 (+166); LR-MS (ESI) *m/z* = 845 (15), 844 (57), 843 (M$^+$, bp), 842 (22); Anal. Calcd for $C_{54}H_{52}N_4B_2F_8 \cdot 2H_2O$: C 67.10, H 5.84, N 5.80. Found: C 67.06, H 5.56, N 5.72.

Preparation of 5,7-dihydro-5,5,7,7-tetrakis(4-dimethylaminophenyl)dibenzo[*b*,*g*][1,5]oxathiocin (4A). To a solution of **4B**$^{2+}$(BF_4^-)$_2$ (99 mg, 0.117 mmol) in MeCN (35 mL) was added aqueous $Na_2S \cdot 9H_2O$ (1.44 mg, 6.00 mmol) (7 mL). The mixture was stirred for 30 min. The resulting suspension was extracted with AcOEt, and the combined organic layer was washed with water and brine. After drying over Na_2SO_4, the solution was filtered through Al_2O_3 pad, and the filtrate was concentrated to give **4A** (60 mg) as a greenish solid in 73% yield.

Data of **4A**: Decomp. 156-157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (m, 10H), 7.00 (ddd, *J* = 7.5 Hz, 7.5, 1.5 Hz, 2H), 6.59 (ddd, *J* = 7.5 Hz, 7.5, 1.5 Hz, 2H), 6.48 (d, *J* = 9.2 Hz, 8H), 6.33 (dd, *J* = 7.5, 1.5 Hz, 2H), 2.88 (s, 24H) ppm; IR (KBr) 2880, 2847, 2794, 1608, 1571, 1561, 1515, 1478, 1439, 1351, 1292, 1267, 1230, 1205, 1160, 1129, 1105, 1059, 948, 819, 802, 791, 762, 747, 575 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 276 (54800); LR-MS (FD) *m/z* = 705 (M$^+$+1, 7), 704 (M$^+$, 13), 393 (28), 399 (bp); HR-MS (FD) calcd. for $C_{46}H_{48}N_4OS$: 704.3549; found: 704.3564.

Preparation of diphenyl ether-2,2'-diylbis[bis(4-dimethylaminophenyl)methylium] bis(tetrafluoroborate) [4B^{2+}(BF_4^-)$_2$]. To a solution of 2,2'-diiododiphenyl ether (410 mg, 972 μmol) in

THF (6 mL) was added dropwise *n*-BuLi (1.65 M hexane solution 2.5 mL, 4.13 mmol) at –78 °C. The mixture was stirred for 1 h at –78 °C, and then 4,4'-bis(dimethylamino)benzophenone (1.11 g, 4.13 mmol) was added as a solid. The mixture was warmed to room temperature and stirred for 12 h. To the mixture was added dropwise *n*-BuLi (1.65 M hexane solution 2.5 mL, 4.13 mmol) to consume the remaining benzophenone at –78 °C. The mixture was warmed to room temperature and stirred for 30 min. After addition of saturated aqueous NH_4Cl, the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine. After drying over Na_2SO_4, the solvent was removed. The residue was purified by chromatography (SiO_2, AcOEt:hexane = 1:2) to give diol (466 mg, 68%) as a light yellow powder.

To a solution of the diol (385 mg, 545 μmol) in THF (23 mL) was added a solution of 42% aqueous HBF_4 (0.23 mL, 1.51 mmol) in THF (2.5 mL). After stirring for 14 h at room temperature, the mixture was diluted with Et_2O. The resulting suspension was filtered to give **4B**$^{2+}$(BF_4^-)$_2$ (399 mg, 87%) as a dark brown powder. The analytical sample was obtained from recrystallization from EtOH.

Data of **4B**$^{2+}$(BF_4^-)$_2$: Decomp. 204-208 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 7.55 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 2H), 7.24 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 8H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 2H), 6.93 (br. d, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 8H), 3.22 (s, 24H); IR (KBr) 1620, 1586, 1474, 1444, 1374, 1230, 1172, 1160, 1124, 1084, 1034, 938, 910, 834, 720, 520, 422 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1}cm^{-1}) 318 (28400), 424 (23600), 638 (137000); LR-MS (FAB) *m/z* = 672 (M$^+$, bp); Anal. Calcd for $C_{48}H_{48}B_2F_8N_4O\cdot C_2H_5OH\cdot H_2O$: C 63.31, H 6.20, N 6.15. Found: C 63.48, H 5.70, N 6.37.

Oxidative transformation of 1A to 1B^{2+}(I_3^-)$_2$. To a solution of **1A** (905 mg, 1.31 mmol) in CH_2Cl_2 (50 mL) was added iodine (1.04 g, 4.10 mmol). After stirring for 24 h at room temperature, the mixture was diluted with Et_2O. The resulting suspension was filtered to give **1B**$^{2+}$(I_3^-)$_2$ (1.73 g, 88%) as a dark purple powder. The filtrate was treated with $P(OMe)_3$ to remove remaining iodine, and chromatophraphic separation (Al_2O_3, Et_2O) gave elemental sulfur (12.9 mg), which corresponds to 31% of the calculated amount according to Scheme 1.

Data of **1B**$^{2+}$(I_3^-)$_2$: Decomp. 198-200 °C; ^{1}H NMR spectrum is idental to (BF_4^-)$_2$ salt; IR (KBr) 1615, 1581, 1477, 1398, 1359, 1168, 1121, 723 cm^{-1}. Anal. Calcd for $C_{46}H_{48}I_6N_4\cdot CH_2Cl_2$: C 37.55, H 3.35, N 3.73. Found: C 37.30, H 3.35, N 3.71.

Oxidative transformation of 4A to 4B^{2+}(I_3^-)$_2$. To a solution of **4A** (20.1 mg, 28.5 μmol) in CH_2Cl_2 (3 mL) was added iodine (22.7 mg, 89.4 μmol). After stirring for 42 h at room temperature, the mixture was diluted with Et_2O. The resulting suspension was filtered to give **4B**$^{2+}$(I_3^-)$_2$ (37.5 mg, 92%) as a dark red powder.

Data of **4B**$^{2+}$(I_3^-)$_2$: Decomp. 180-182 °C; ^{1}H NMR spectrum is idental to (BF_4^-)$_2$ salt; IR (KBr) 2916, 2360, 1616, 1581, 1470, 1440, 1358, 1227, 1164, 938, 909, 827, 719 cm^{-1}; Anal. Calcd for $C_{46}H_{48}I_6N_4O \cdot CH_2Cl_2$: C 37.16, H 3.32, N 3.69. Found: C 37.37, H 3.26, N 3.43.

X-Ray analyses. Crystal data of **1A**: MF $C_{46}H_{48}N_4S$, FW 688.97, monoclinic *P*21/c, a = 18.602(6), b = 8.575(3), c = 23.460(8), β = 91.898(2)°, V = 3740.2(1) Å^3, ρ(Z = 4) = 1.223 g cm^{-3}, *T* = 153 K, R = 13.63%, GOF = 1.228. CCDC 843534. Crystal data of **3A** Crystal data of **6**: MF $C_{54}H_{52}N_4S$, FW 827.08, monoclinic *P*21/c (No. 14), a = 11.161(3), b = 31.378(6), c = 13.276(3), β = 114.500(3)°, V = 4230.9(15) Å^3, ρ(Z = 4) = 1.239 g cm^{-3}, *T* = 150 K, R = 7.09%, GOF = 1.077. CCDC 1493068. Crystal data of **4A**·hexane: MF $C_{49}H_{55}N_4SO$, FW 748.06, triclinic *P*-1, a = 10.789(3), b = 12.567(4), c = 16.154(5), α = 88.843(11), β = 79.117(10), γ = 69.790(8)°, V = 2016.0(9) Å^3, ρ(Z = 2) = 1.232 g cm^{-3}, *T* = 150 K, R = 7.18%, GOF = 1.146. CCDC 1493067.

Cyclic voltammetry. The voltammetric analyses were conducted in MeCN containing 0.1 M Et_4NClO_4 as a supporting electrolyte (*E* / V vs SCE, Pt electrode, scan rate 100 mV s^{-1}). The oxidation wave is irreversible in all cases, and the oxidation potentials were estimated as E^{peak} - 0.03 V. Ferrocene undergoes one-electron oxidation at +0.38 V under the similar conditions.

ACKNOWLEDGEMENTS

We thank Grant-in-Aid for Scientific Research on Innovative Areas: “Middle molecular strategy” (No. 2707) from MEXT and Grant-in-Aid from JSPS (Nos. 15H03790, 16K13968, 16H0659106) Japan. This work was also supported by the Cooperative Research Program of “Network Joint Research Center for Materials and Devices”.

REFERENCES AND NOTES

1. K. Šindelář, J. Holubek, M. Ryska, I. Koruna, and M. Protiva, *Coll. Czech. Chem. Commun.*, 1986, **51**, 2848.
2. W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, 1956, **78**, 6130.
3. T. Murai, *Pure Appl. Chem.*, 2010, **82**, 541; F. Shibahara and T. Murai, *J. Synth. Org. Chem. Jpn.*, 2011, **69**, 28; R. Sato, *Heteroat. Chem.*, 2007, **18**, 482.
4. *TTF Chemistry*, ed. by J.-i. Yamada and T. Sugimoto, Springer, Heidelberg, 2004; T. Otsubo and K. Takimiya, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 43; S. Ogawa, *J. Synth. Org. Chem. Jpn.*, 2004, **62**, 140.
5. E. Block, *Oxidation and Reduction of Sulphides*, In *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues*, pp. 539-608, ed. by S. Patai, John Wiley & Sons,

Chichester, 1980.

6. H. W. Zappey, S. Ingenamm, and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1887.
7. T. Suzuki, H. Tamaoki, K. Wada, R. Katoono, T. Nehira, H. Kawai, and K. Fujiwara, *Chem. Commun.*, 2012, **48**, 2812.
8. T. Suzuki, T. Kuroda, H. Tamaoki, S. Higasa, R. Katoono, K. Fujiwara, T. Fukushima, and H. Yamada, *Chem. Lett.*, 2013, **42**, 706.
9. X. Z. Qin, Q. C. Meng, and F. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6778; M. Kamata, K. Murayama, T. Suzuki, and T. Miyashi, *Chem. Commun.*, 1990, 827; M. Puiatti, J. E. Argüello, and A. B. Peñéñory, *Eur. J. Org. Chem.*, 2006, 4528.
10. E. Baciocchi, E. Fasella, O. Lanzalunga, and M. Mattioli, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1071.
11. T. Suzuki, J. Nishida, and T. Tsuji, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1329.
12. C. W. Looney and W. T. Simpson, *J. Am. Chem. Soc*., 1954, **76**, 6293.
13. T. Suzuki, H. Tamaoki, J. Nishida, H. Higuchi, T. Iwai, Y. Ishigaki, K. Hanada, R. Katoono, H. Kawai, K. Fujiwara, and T. Fukushima, *Chapter 2 Redox-mediated reversible σ-bond formation/cleavage,* In *Organic Redox Systems: Synthesis, Properties and Applications*, pp. 13-38, ed. by T. Nishinaga, Wiley, 2015; T. Suzuki, E. Ohta, H. Kawai, K. Fujiwara, and T. Fukushima, *Synlett*, 2007, 851; T. Suzuki, H. Higuchi, T. Tsuji, J. Nishida, Y. Yamashita, and T. Miyashi, *Chapter 1: Dynamic Redox Systems*, In *Chemistry of Nanomolecular Systems*, pp. 3-24, ed. by T. Nakamura, T. Matsumoto, H. Tada, and K.-i. Sugiura, Springer, Heidelberg, 2003.
14. G. A. Jeffrey and A. Robbins, *Acta Crystallogr.*, 1980, **B36**, 1820.
15. N. Asakura, S. Fujimoto, N. Michihata, K. Nishii, H. Imagawa, and H. Yamada, *J. Org. Chem.*, 2011, **76**, 9711.
16. T. Ohta, M. Ito, K. Inagaki, and H. Takaya, *Tetrahedron Lett.*, 1993, **34**, 1615; H. Hocke and Y. Uozumi, *Tetrahedron*, 2003, **59**, 619; T. Suzuki, Y. Ishigaki, T. Iwai, H. Kawai, K. Fujiwara, H. Ikeda, Y. Kano, and K. Mizuno, *Chem. Eur. J.*, 2009, **15**, 9434.
17. The X-ray analysis was conducted for racemate with a higher crystallinity. The sample of *rac*-**3A** was obtained upon treating *rac*-**3B**$^{2+}$(BF_4^-)$_2$ with Na_2S in 76% yield.
18. R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1976, 913.
19. *Electrochromism and Electrochromic Devices*, ed. by P. M. S. Monk, R. J. Mortimer, and D. R. Rosseinsky, Cambridge Univ. Press, Cambridge, 2007.
20. *Circular Dichroism: Principles and Applications*, 2nd edn., ed. by N. Berova, K. Nakanishi, and R. W. Woody, Wiley-VCH, New York, 2000.
21. In the case of $PhAr_2C$-S-CAr_2Ph **5A**, an acyclic analogue of the heterocycles obtained by MG^+ (2

equiv.) and Na_2S, the electrochemical oxidation directly caused the gradual raise of the absorption of MG^+ as expected, since the first C–S mesolysis of **5A**$^{+\bullet}$ generates MG^+ (ref. 8).

22. P. Maslak and J. Theroff, *J. Am. Chem. Soc.*, 1996, **118**, 7235.
23. B. van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, 1977, **99**, 6806; B. van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, 1977, **99**, 6810.
24. R. J. Goldacre and J. N. Phillips, *J. Chem. Soc*., 1949, 1724.