

# Conjugation-extended ring assemblies with central heterocycles. New multistage redox systems

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**Abstract** - A series of redox-active conjugation-extended ring assemblies involving one or more central five-membered or related heterocycles has been synthesized and characterized. These compounds, in contrast to the corresponding open-chain polyene- or phenylene-bridged systems, maintain an enhanced conjugative interaction among the bridging and terminal rings, and a rigid and coplanar conformation throughout the redox process, generating thermodynamically stable radical ions as well as doubly ionized species, which are quite favorable as redox reagents. Consequently, valuable experimental results to clarify the mechanisms of redox reactions of conjugation-extended systems have been revealed. Moreover, currently interesting properties such as a novel amphoteric three-stage or four-stage redox reaction, a relatively high conductivity for the complexes of extended TTF derivatives, a strong fluorescence emission for doubly ionized species, and a unique electrochromism for extended viologens have been observed and these are discussed in detail.

## 1 INTRODUCTION

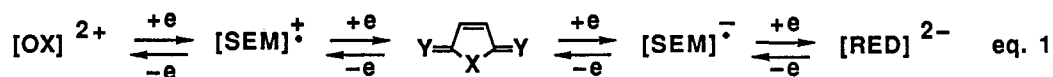
Molecular design and synthesis of novel multistage redox systems exhibiting electrochemical and physical properties of remarkable interest have been keenly desired to ensure versatile development of material science and material technology which are closely concerned with molecular electronics.

Especially the conjugation-extended type of redox system has attracted current interest, and many papers dealing with various types of extended redox systems have recently been published mainly in the search for promising electron donors or acceptors for organic metals, since the conjugation-extension by introducing a  $\pi$ -framework between the two terminal redox active centers of the traditional Wurster and Weitz type redox systems has been known to stabilize the dication and dianion states by reducing the intramolecular Coulomb repulsive energy (ref. 1). Moreover, conjugation-extended redox reagents exhibiting an intense absorption maximum in the visible or near-infrared region in their electronic spectrum and/or showing reversible and remarkable color change on application and removal of an electric voltage or current would have high utility potential for new electrochromic display devices, optical storage media (ref. 2), or other materials with extended performances (ref. 3).

Although active investigation has been continued, many of the extended-type of redox reagents so far synthesized are rather unstable in neutral states and tend to give unstable radical ions undergoing a one-step two-electron redox reaction as have been observed in the extended TTF analogues having a 1,4-butenediylidene (ref. 4), benzoquinonoid (ref. 5), or naphthoquinonoid (ref. 6) linking group. Therefore, a molecular design strategy advantageous in stabilizing both neutral and ionic species including radical ions (ref. 7) has been sought in the research in this area. In this article a new molecular design strategy meeting these requirements has been proposed.

We have already designed and synthesized different kinds of quinarenoid compounds (ref. 8) and in these efforts have clarified that a dihydrothiophenediylidene (thienoquinonoid) or dihydrofurandiylidene (furanquinonoid) moiety is highly effective as compared with a polyethenediylidene or benzoquinonoid moiety as a linking  $\pi$ -framework to stabilize the quinarenes and quinarenones (ref. 9, 10). This finding prompted study on the design and synthesis of several new types of conjugation-extended redox systems, namely, extended quinones, extended TTF, and extended viologen analogues incorporating one or more

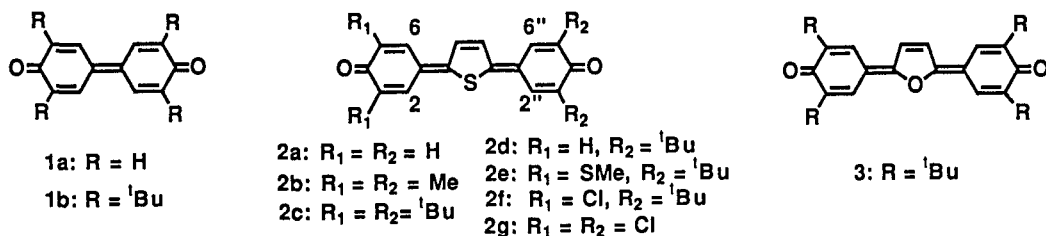
central five-membered and related heterocycles. These conjugation-extended redox systems maintain rigid and coplanar conformations throughout the redox process (eq. 1) in which thermodynamically stable radical ions as well as doubly ionized ions are involved.



In consequence, aspects of the highly conjugation-extended redox systems which were not well understood so far have been clarified, and valuable properties such as amphoteric three-stage or four-stage redox reactions for highly extended quinones up to a sexiphenoquinone analogue, a relatively high electroconductivity for the complexes of the extended TTF derivatives, a unique electrochromism for the extended viologens and a strong fluorescence emission for the dications and the dianions, and so on, have been observed. It is on these aspects that the following discussions are focused.

## 2 EXTENDED QUINONES INVOLVING A CENTRAL HETEROCYCLIC LINKING GROUP

Although a series of quinones has been most thoroughly investigated and widely used so far, the series has been mainly limited to the dioxo derivatives of aromatic hydrocarbons. We have synthesized new terphenylquinone analogues **2a–c** involving a central heterocyclic quinonoid ring as a key skeletal component (ref. 11) via 2-(4-alkoxyphenyl)thiophene and 2,5-bis(4-alkoxyphenyl)thiophene conveniently prepared by using palladium (0)-catalyzed cross-coupling reaction of 4-alkoxyaryl halides with thienylzinc chloride and related reactions. More recently, **2d–g** have also been synthesized (ref. 12).



These quinones are stable in the solid state and in solution. Judging from the magnetic nonequivalency of the six-membered ring protons and carbons between those on the same side (H-2,2'') and on the opposite side (H-6,6'') to the central sulfur atom in the NMR spectra, the rotation of the terminal six-membered rings about the intercyclic bonds does not take place in **2** at ordinary temperature in solution. From X-ray crystallographic analysis (Fig. 1), **2c** has been shown to exist in a coplanar conformation in the solid state in which the terminal six-membered rings incline 9.1° and 11.1°, respectively, from the mean plane of the central five-membered ring, and the twisting angle between the mean planes of the two terminal rings is 1.8°.

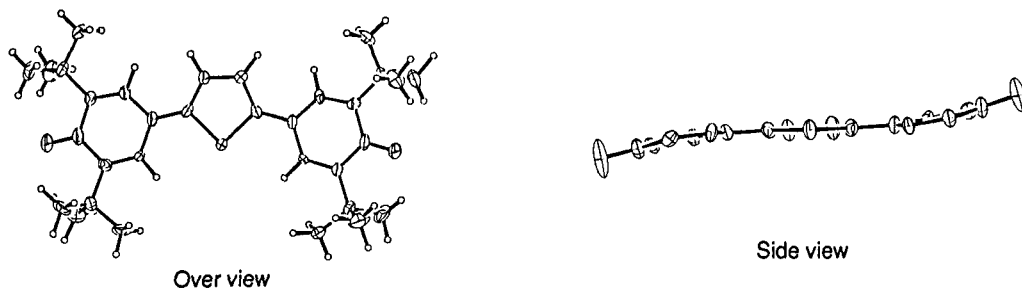


Fig. 1. Molecular structure (ORTEP) of **2c**.

Quinones **2b–g** can be reduced reversibly in two successive one-electron-transfer reactions up to the dianions via the stable anion radicals, and, more interestingly, oxidized reversibly to the radical cations. The electrochemical data of **2a–c** obtained by the CV are summarized in Table 1. On considering the poor electron donating ability of the corresponding diphenylquinones **1a,b**, it is noticeable that **2** is easily oxidized in the potential range of 1.10–1.71 V. Thus, **2** are characterized as a new type of quinones exhibiting an amphoteric three-stage redox behavior, except the dimethylthio derivative **2e** which shows an amphoteric four-stage redox behavior.

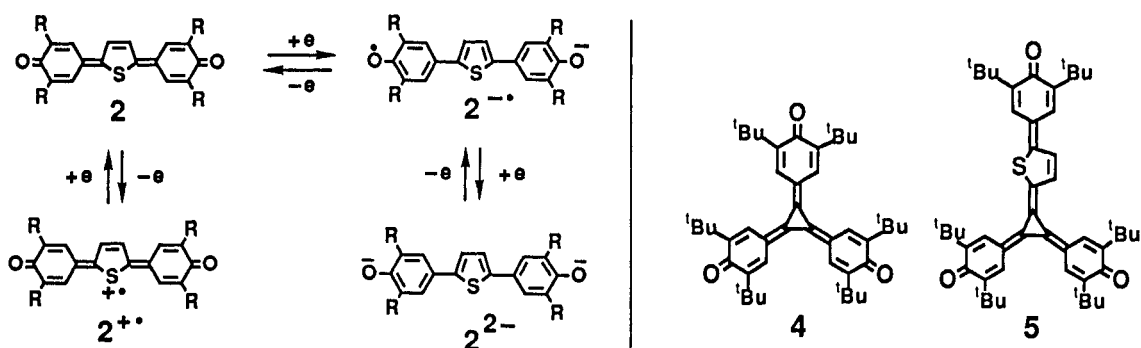
TABLE 1. Electrochemical properties<sup>a</sup> of 1a, 2a–2c, 2e, and 2g.

Compound	Solvent	E <sub>2</sub> <sup>ox</sup>	E <sub>1</sub> <sup>ox</sup>	E <sub>1</sub> <sup>red</sup>	E <sub>2</sub> <sup>red</sup>	E <sub>1</sub> <sup>sum</sup>	E <sub>2</sub> <sup>sum</sup>
1a	MeCN	---	---	-0.23	-0.52	---	---
2a	C <sub>6</sub> H <sub>5</sub> CN	---	+1.46	-0.12	-0.22	1.58	---
2b	C <sub>6</sub> H <sub>5</sub> CN	---	+1.21	-0.37	-0.44	1.58	---
2c	C <sub>6</sub> H <sub>5</sub> CN	---	+1.23	-0.47	-0.67	1.70	---
2e	C <sub>2</sub> H <sub>5</sub> CN	+1.45	+1.10	-0.31	-0.49	1.41	1.94
2g	C <sub>2</sub> H <sub>5</sub> CN	---	+1.71	+0.11	+0.01	1.82	---

a: Obtained by cyclic voltammetry: 0.1 mmol dm<sup>-3</sup> in MeCN with 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> at room temperature, scan rate : 50 mV s<sup>-1</sup>, V vs. SCE.

The amphoteric redox property of 2a–g can be ascribed to the significant decrease in the HOMO–LUMO separation which resulted from the thienoquinonoid extension, e.g. the HOMO and the LUMO of 2a lie at a higher level by 0.97 eV and at a lower level by 0.15 eV, respectively, than the corresponding MO's of 1a. From the EPR study on 2c<sup>•+</sup>, it is shown that the unpaired electron of the radical cation delocalizes considerably on the sulfur atom, since the g value of 2c<sup>•+</sup> (2.0055) is significantly larger than that of 2c<sup>•-</sup> (2.003). Therefore, the amphoteric three-stage redox reaction of 2 proceeds according to the sequence shown in Scheme 1. Rotation of the terminal rings about the intercyclic bonds appears not to occur in the radical cation species because H-2,2'' and H-6,6'' are nonequivalent in the EPR spectra of 3<sup>•+</sup> (ref. 13) whereas they are equivalent in 2c<sup>•+</sup>. The first reduction potential (E<sub>1</sub><sup>red</sup>) and the first oxidation potential (E<sub>1</sub><sup>ox</sup>) showed a linear correlation with Σσ<sub>p</sub> and Σσ<sub>p</sub><sup>+</sup>, respectively, but the substituent effect is not so sensitive, giving a relatively poor linearity in the latter case as compared with the former.

Scheme 1



The thienoquinonoid-extension method could be applicable more widely to the molecular design strategies for synthesizing amphoteric compounds, since thienoquinonoid-extended [3]radialene derivative 5 (ref. 14) showed an amphotericity (E<sub>1</sub><sup>sum</sup> = 1.07) even though the electron-accepting ability of the mother compound 4 (ref. 15) is as strong as that of chloranil. Compound 5 is the first radialene exhibiting an amphoteric redox property. The E<sub>1</sub><sup>red</sup> of 5 is much more positive by 0.5 V than that of 2c and is almost equal to that of 4. The E<sub>p</sub><sup>ox</sup> of 5 is lower by about 0.1 V than that of 2c, whereas the former involves one more quinonoid carbonyl group than the latter. Thus, 5 displayed a higher amphotericity exhibiting the E<sub>1</sub><sup>sum</sup> value smaller by 0.59 V than that for 2c.

### 3 EXTENDED QUINONES INVOLVING A CENTRAL OLIGOTHIENYL LINKING GROUP

Highly amphoteric organic molecules (ref. 16) have attracted much attention in recent years in the search for single-component organic conductors (ref. 17). We have synthesized and isolated in solid state highly extended quinones 6, 7, and 8 (ref. 18) as the first example of quater-, quinque-, and sexiphenoquinone analogues in which the inner cyclohexadienediylidene are replaced by dihydrothiophenediylidene. These compounds undergo two-stage one-electron reductions and two-stage one-electron oxidations, whereas the second oxidation step is irreversible. From the EPR study the radical anion and radical cation generated from 6 were proved to be very stable species. The E<sub>1</sub><sup>red</sup> increases in the order of 6 < 7 < 8 and the E<sub>1</sub><sup>ox</sup> does so in the reverse order (Table 2). The same trend is observed for the E<sub>2</sub><sup>red</sup> and E<sub>2</sub><sup>ox</sup>. Consequently,

the  $E_1^{\text{sum}}$  and  $E_2^{\text{sum}}$  become smaller in the order of  $6 > 7 > 8$ . The  $E_1^{\text{sum}}$  of **8** (0.75 V) is the smallest value of all closed-shell organic compounds previously reported. The decreasing order of the HOMO – LUMO gap is actually revealed by the first excitation band being in bathochromic shift in the order of  $6 < 7 < 8$  in their electronic spectra. Quinones **6** and **7** are useful as write-once optical storage media sensitive to semiconductor laser light, since they have a very strong absorption band in a near IR range and can be made into thin films with high reflectivities.

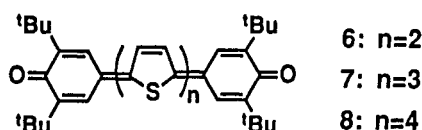


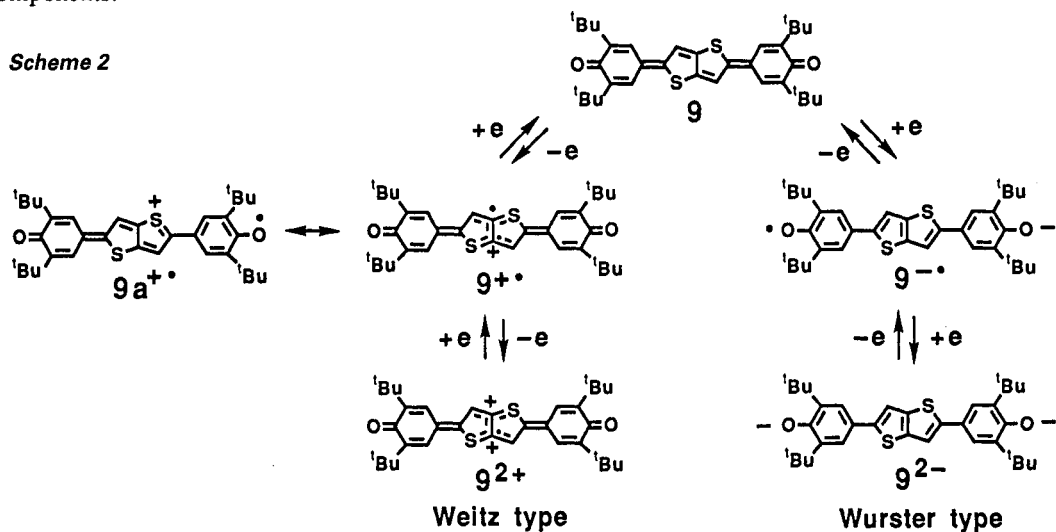
TABLE 2. Electrochemical properties<sup>a</sup> and the longest wavelength absorption maximum<sup>b</sup> of **6**, **7**, and **8**.

Compd.	Solvent	$E_2^{\text{ox}}$	$E_1^{\text{ox}}$	$E_1^{\text{red}}$	$E_2^{\text{red}}$	$E_1^{\text{sum}}$	$E_2^{\text{sum}}$	$\lambda$ /nm (og $\epsilon$ )
<b>6</b>	C <sub>6</sub> H <sub>5</sub> CN	+1.37	+0.85	-0.36	-0.50	1.21	1.87	678 (4.50)
<b>7</b>	C <sub>2</sub> H <sub>5</sub> CN	+1.07	+0.63	-0.26	-0.30	0.89	1.37	785 (4.77)
<b>8</b>	C <sub>2</sub> H <sub>5</sub> CN	+0.89	+0.55	-0.20	-0.26	0.75	1.15	830 (4.45)

a: Obtained by cyclic voltammetry: 0.1 mmol dm<sup>-3</sup> in MeCN with 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> at room temperature, scan rate : 50 mV s<sup>-1</sup>, V vs. SCE. b: In MeCN.

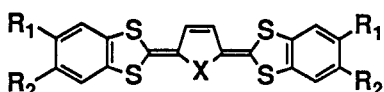
#### 4 EXTENDED QUINONES INVOLVING A CENTRAL DITHIAPENTALENE LINKING GROUP

There has so far been no report on closed shell amphoteric four-stage redox systems involving different redox-active units, in which a single molecule is both anodically oxidized in a Weitz type manner and cathodically reduced in a Wurster type one (ref. 19). We have now synthesized compound **9** (ref. 20) and have demonstrated that **9** can be categorized as the first example in this new mode of redox system. The two oxygen atoms bearing the bulk of the negative charge in  $9^{2-}$  are well separated and behave as the end groups of the Wurster type reduction process since the  $\Delta E^{\text{red}}$  of **9** (0.13 – 0.10 V) is smaller than those of **1b** and **2c**, indicating a smaller Coulomb repulsion in  $9^{2-}$  than in  $1^{2-}$  and  $2c^{2-}$ . On the other hand, the two central sulfur atoms should function as the end groups of the Weitz-type oxidation sequence, since the  $\Delta E_p^{\text{ox}}$  value (0.50 – 0.52 V) is far larger than the  $\Delta E^{\text{red}}$  value in **9** and is even larger than the  $\Delta E^{\text{ox}}$  of TTF (0.33 V), indicating the significantly increased Coulomb repulsion in  $9^{2+}$ . The bulk of the spin population in  $9^{+}$  resides on the sulfur atoms, since the  $g$  value of  $9^{+}$  (2.0055) is substantially larger than that of  $9^{\cdot+}$  (2.0035) in their EPR spectra. Therefore, the amphoteric four-stage redox reaction of **9** proceeds according to the sequence shown in Scheme 2, involving both the Wurster type reduction and the Weitz type oxidation although the galvinoxyl structure may contribute to  $9^{+}$  to a limited extent. This kind of redox system would be of current interest in its possibilities for the creation of novel conducting complexes with three interacting components.



## 5 CONJUGATION-EXTENDED TTF ANALOGUES INVOLVING A CENTRAL HETEROCYCLIC LINKING GROUP

TTF type of donors with extended  $\pi$ -conjugation are promising electron donors for organic metals, but those extended by a linking bridge consisting of more than two  $sp^2$  carbons (ref. 4), or those extended by a benzoquinonoid bridge (ref. 5, 6) have been found to give unstable radical cations, for which no single electron nature has been observed in their redox reactions as mentioned before. Thus, the discussion has been focused on the point how the radical ions can be thermodynamically stabilized in these extended TTF systems, since the high conductivity is essentially associated with the radical cation state of the stacks. A new molecular design strategy to stabilize the radical cations of conjugation-extended TTF systems, that is, the incorporation of a heterocyclic linking group, has now been proposed.



10 : X=S, R<sub>1</sub>=R<sub>2</sub>=H

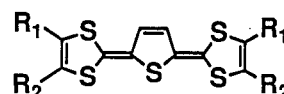
11 : X=S, R<sub>1</sub>=H, R<sub>2</sub>=Me

12 : X=S, R<sub>1</sub>=R<sub>2</sub>=Me

13 : X=O, R<sub>1</sub>=R<sub>2</sub>=H

14 : X=O, R<sub>1</sub>=H, R<sub>2</sub>=Me

15 : X=O, R<sub>1</sub>=R<sub>2</sub>=Me



16 : R<sub>1</sub>=R<sub>2</sub>=H

17 : R<sub>1</sub>=R<sub>2</sub>=Me

18 : R<sub>1</sub>=H, R<sub>2</sub>=Ph

Extended DBTTF analogue **10** and its alkyl derivatives **11** and **12** (ref. 21) synthesized according to this concept are quite stable in the solid state and in solution, and showed two well-defined reversible one-electron oxidation waves in their cyclic voltammograms. The thermodynamic stability of the radical cations **10**<sup>•+</sup>, **11**<sup>•+</sup>, and **12**<sup>•+</sup> is clearly demonstrated by the relatively large log  $K_{sem}$  values of around 4.07. Moreover, **10**–**12** appear to be promising donors for TCNQ, since the donor ability increases by 0.31 V – 0.37 V compared with that of DBTTF, being nearly comparable with that of TTF (0.38 V). Indeed, all of these extended DBTTF containing a heterocyclic linking group gave stable complexes with TCNQ and DDQ, and gave radical salts with iodine, whose resistivities at room temperature on their compressed pellets are listed in Table 3. The resistivity of the DDQ complexes of **10**, **11**, and **12** are  $10^3$ – $10^2$  times lower than those of benzoquinonoid-extended Me<sub>2</sub>DBTTF (ref. 22), probably due to the thermodynamic stability of the radical cations. The TCNQ complexes of **10** and **11** would be in partial CT conditions with the degree of CT,  $Z = 0.70$ – $0.75$ , and indeed show  $10^4$ – $10^5$  times lower resistivities than that of DBTTF. It is also clarified that the methyl substitution causes a decrease in the resistivity of the complexes. The electronic properties of the furanoquinonoid-extended DBTTF's **13**, **14**, and **15** are nearly comparable with those of **10**, **11**, and **12**, respectively (ref. 23).

TABLE 3. Electrochemical properties<sup>a</sup> of conjugation-extended donors and resistivities<sup>b</sup> of their complexes.

Donors	Electrochemical property			resistivity $\rho/\Omega\text{cm}$		
	$E_{1^{ox}}$	$E_{2^{ox}}$	log $K_{sem}$	TCNQ (1:1)	DDQ (1:1)	$I_x$ (ratio)
<b>10</b>	+0.34	+0.58	4.07	$1.2 \times 10^2$	$6.4 \times 10^3$	$2.7 \times 10^6$ (1 : 3.0)
<b>11</b>	+0.30	+0.54	4.07	$4.9 \times 10$	$5.5 \times 10^2$	$3.0 \times 10^4$ (1 : 3.5)
<b>12</b>	+0.28	+0.52	4.07	----	$6.3 \times 10^2$	$4.8 \times 10^2$ (1 : 4.3)
<b>13</b>	+0.35	+0.57	3.73	$3.3 \times 10^2$	----	$3.9 \times 10^5$ (1 : 5.5)
<b>14</b>	+0.31	+0.53	3.73	$1.1 \times 10^3$	----	$1.1 \times 10^4$ (1 : 6.3)
<b>15</b>	+0.28	+0.50	3.73	$1.2 \times 10$	----	$1.6 \times 10^3$ (1 : 4.3)
DBTTF	+0.65	+1.00	5.93	$5.4 \times 10^6$	58	$1.4 \times 10^8$ (1 : 3.0)
<b>17</b>	+0.04	+0.31	4.58	80 (1 : 2)	$7.8 \times 10^6$ (1 : 2)	8.2 (1 : 2.1)
<b>18</b>	+0.09	+0.40	5.25	----	$7.1 \times 10^6$ (1 : 2)	300 (1 : 1.6)

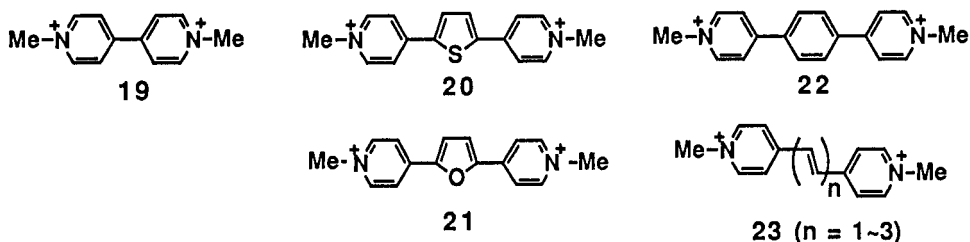
a: Obtained by cyclic voltammetry: 0.1 mmol dm<sup>-3</sup> in MeCN with 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> at room temperature, scan rate: 50 mV s<sup>-1</sup>, V vs. SCE. b: Compressed pellets by two-probe technique at room temperature.

Tetramethyl and diphenyl derivatives **17** and **18**, isolated in their dication forms (ref. 24), also compose a reversible two-stage one-electron redox system exhibiting relatively large log  $K_{sem}$  values. The complex [17<sup>•+</sup>(TCNQ)<sub>2</sub>] showed more than 10 times lower resistivity than the TCNQ complexes of the corresponding naphthoquinonoid- and benzoquinonoid-extended TMTTF (ref. 25, 26). The complexes [17<sup>•+</sup>(I)<sub>2</sub>] and [18<sup>•+</sup>(I)<sub>1</sub>] showed  $10^5$ – $10^3$  times lower resistivity than that of the iodine complexes of benzoquinonoid- or naphthoquinonoid-extended Ph<sub>2</sub>TTF (ref. 26, 27). The excessive electron donating

property of the donors **17** and **18** inhibits formation of 1:1 complexes with TCNQ. But the  $[17 \cdot (\text{TCNQ})_2]$  appears to be in a partial CT condition with mixed valence since the complex exhibits a relatively low resistivity and show two CN stretching bands at 2170 and 2190  $\text{cm}^{-1}$  in the IR spectrum. The  $[17 \cdot (\text{I})_2]$  showed a very low resistivity which is the lowest recorded value so far for the complexes of conjugation-extended type of TTF and DBTTF with iodine. More recently, unsubstituted donor **16** has been synthesized as reddish-violet crystals (ref. 23). The single crystal growings for these CT complexes and radical salts are now in progress to clarify the crystal structures.

## 6 EXTENDED VIOLOGENS INVOLVING A CENTRAL HETEROCYCLIC LINKING GROUP

Viologens are the most prototypical Weitz type redox reagent used widely in various fields of pure and applied chemistry (ref. 28, 29). Viologens of conjugation-extended types have recently attracted interest as intramolecular long-distance electron transfer mediators in the conversion of photoenergy into chemical energy (ref. 30) and as promising candidates for the functional elements of molecular electronic devices (ref. 31). For a novel approach to built-up new conjugation-extended viologens, three-ring assembling viologens **20**, **21**, and **22** have been synthesized (ref. 32).



From the X-ray structural analysis, **20** is shown to exist in a good coplanar conformation (Fig. 2).

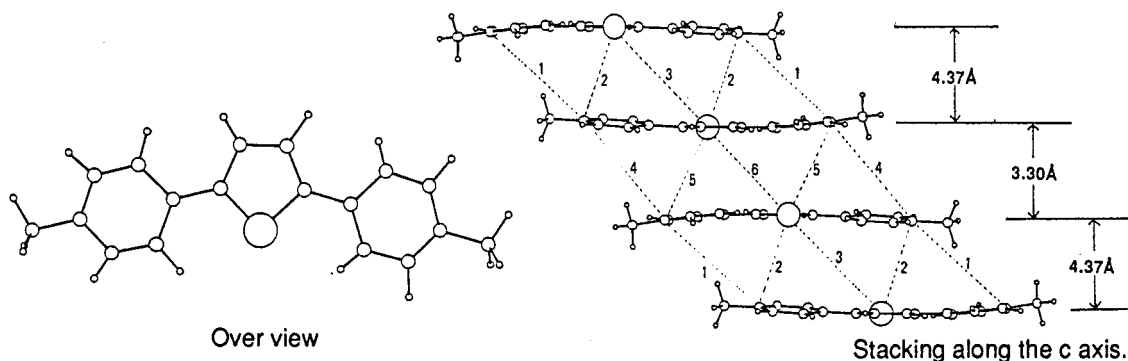


Fig. 2. Molecular structure (ORTEP) and crystal structure of **20**.

Viologens **20** and **21** undergo reversible two-stage one-electron reductions (Table 4) indicating the formation of stable radical cations  $20^{+\cdot}$  and  $21^{+\cdot}$  as well as the corresponding neutral species. These

TABLE 4. Electrochemical properties<sup>a</sup> of **20** – **22**, and reference compounds **19** and **23**.

Compound	$E_1^{\text{red}}$	$E_2^{\text{red}}$	$\Delta E$	$\log K_{\text{sem}}$
<b>19</b> (R=Me)	-0.43	-0.85	0.42	7.12
<b>20</b>	-0.69	-0.84	0.15	2.54
<b>20</b> (N+CH <sub>2</sub> CN)	-0.43	-0.55	0.12	2.03
<b>21</b>	-0.74	-0.93	0.19	3.22
<b>22</b>	-0.91 (2e)		=0.0	—
<b>23</b> (n=2)	-0.59 (2e)		=0.0	—

a: Obtained by cyclic voltammetry: 0.1 mmol dm<sup>-3</sup> in MeCN with 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> at room temperature, scan rate : 50 mV s<sup>-1</sup>, V vs. SCE.

properties of **20** and **21** are noteworthy since **22** and vinylogous viologen **23** ( $n = 2$  and  $3$ ) (ref. 28) undergo a one-stage two-electron reduction. The  $E_1^{\text{red}}$  values of **20** and **21** are more negative by about  $0.26 - 0.31$  V than that of methylviologen **19**, but these values can be easily made more positive by introducing slightly more electron-withdrawing substituents such as cyanomethyl groups on the N-atoms (Table 4).

The radical cations **20**<sup>•+</sup> and **21**<sup>•+</sup>, obtained by the one-electron reduction of **20** and **21** with Na-Hg, showed a characteristic low-energy A band in their electronic spectra at 1047–1124 nm and a higher-energy B band at 568–561 nm (Fig. 3) which are more bathochromic by 440–517 nm and 171–167 nm, respectively, compared with those of **19**<sup>•+</sup>. Thus, it should be possible to use **20** and **21** as novel electrochromic display systems in which coloration is brought about by the most intense B band in the visible region or sensitive to semiconductor laser light owing to the A band in the near infrared region.

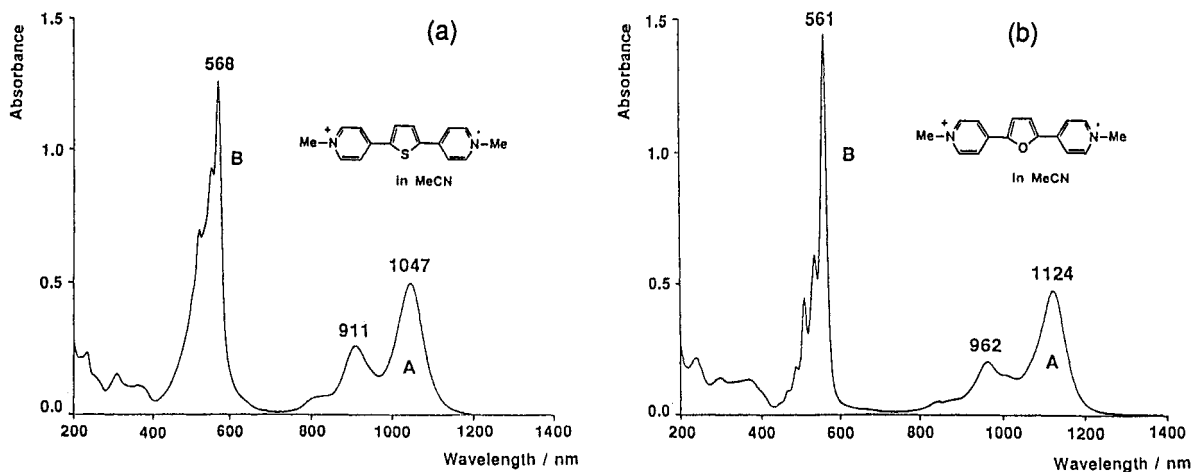


Fig. 3. Electronic spectra of radical cations of (a) **20**<sup>•+</sup> and (b) **21**<sup>•+</sup>, in MeCN.

## 7 PHOTOPHYSICAL PROPERTIES OF THE DOUBLY IONIZED SPECIES OF THE REDOX SYSTEMS EXTENDED BY HETEROCYCLES

Extended viologens **20**, **21**, and **22** showed fluorescence emission spectra upon photoexcitation at room temperature, whereas open-chain-extended **23** are nonfluorescent. As shown in Table 5, the fluorescence maxima at the shortest wavelength corresponding to the  $0 - 0$  transition were shifted to a longer wavelength region on going from **22** to **20** or **21**.

TABLE 5. Photophysical properties of conjugation-extended viologens, **20**, **21**, and **22** in MeCN.

Compound	Excitation $\lambda_{\text{max}}/\text{nm}$	Fluorescence $\lambda_{\text{max}}/\text{nm}$	Life time $\tau_f/\text{ns}$	Quantum yield <sup>a</sup> $\Phi_f$	$k_r$ <sup>b</sup> / $\text{s}^{-1}$ $\times 10^{-8}$	$k_{nr}$ <sup>b</sup> / $\text{s}^{-1}$ $\times 10^{-8}$
<b>21</b>	368, 384	412, 426	1.71	0.84	4.92	0.94
<b>20</b>	369, 385sh	417, 427	1.55	0.75	4.85	1.61
<b>22</b>	318	375	1.17	0.69	5.92	2.66

a: Determined by the comparison of the integrated emission area across the band of the samples with that of perylene in benzene ( $\Phi_f = 0.99$ ). b: Radiative or non-radiative rate constant.

Experimentally determined fluorescence quantum yields ( $\Phi_f$ ) are very high in **20** and **21**, and relatively low in **22**. These findings will open a new route for using these extended viologens for valuable water-soluble lasing dyes (ref. 33). Fluorescence emission has also been observed in the dianions of extended-quinones **2**, **6**, and **9**, and the dication of extended-TTF, **16**. From these facts, it is evident that the dianions and the dications exist in a coplanar conformation not only in the solid state but also in solution.

## 8 CONCLUSION

In the present article, it is shown that the conjugation-extension by incorporating heterocyclic linking group is highly effective in stabilizing the radical ion species as well as neutral and doubly ionized species in the

redox reactions. In consequence, we were able to advance our comprehension of the series of highly conjugation-extended redox systems. The concept of the heterocycle-incorporation could be widely applicable to the molecular design and synthesis of other related systems, opening up many possibilities for the creation of a variety of functionally new type of molecules with significant novel properties.

### Acknowledgement

I am deeply grateful to my coworkers who are mentioned as coauthors in the references. I express my sincere appreciation to Professor Emeritus Tetsuo Nozoe for his encouragement of our study. A part of the present work was supported by a Grant-in-Aid for Scientific Research No. 03640433 from the Ministry of Education, Science and Culture of Japan.

### REFERENCES

1. M. Sato, M. V. Lakshmikanthan, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, **43**, 2084 (1978); Z. Yoshida, T. Kawase, H. Awaji, I. Sugimoto, T. Sugimoto, and S. Yoneda, *Tetrahedron Lett.*, **24**, 3469 (1983); M. R. Bryce, *J. Chem. Soc. Perkin Trans. 1*, 1675 (1985).
2. J. Fabian, R. Zahradnik, *Angew. Chem., Int. Ed. Engl.*, **28**, 677 (1989); J. Fabian, H. Hartmann, *Light Absorption of Organic Colorants*, Springer, (1980); M. Maeda, *Laser Dyes. Properties of Organic Compounds for Dye Lasers*, Academic Press, New York (1984).
3. J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **29**, 1304 (1990); R. Brettle, D. A. Dunmur, N. J. Hindley, and C. M. Marson, *J. Chem. Soc., Chem. Commun.*, 410 (1992).
4. Z. Yoshida, T. Kawase, H. Awaji, and S. Yoneda, *Tetrahedron Lett.*, **24**, 3473 (1983).
5. Y. Yamashita, Y. Kobayashi, and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, **28**, 1052 (1989).
6. A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 157 (1991).
7. M. R. Bryce, E. Fleckenstein, and S. Hünig, *J. Chem. Soc., Perkin Trans. 2*, 1777 (1990).
8. K. Takahashi, S. Takenaka, and T. Nozoe, *Tetrahedron*, **30**, 2191 (1974); K. Takahashi, F. Ishikawa, and K. Takase, *Tetrahedron Lett.*, 4655 (1976); K. Takahashi and K. Takase, *Tetrahedron Lett.*, 245 (1975).
9. K. Takahashi, K. Takase, and T. Sakae, *Chem. Lett.*, 1485 (1980); K. Takahashi, T. Sakae, and K. Takase, *Chem. Lett.*, 179 (1980); K. Takahashi, K. Nishijima, K. Takase, and S. Katagiri, *Tetrahedron Lett.*, **24**, 205 (1983).
10. K. Takahashi, *J. Synth. Org. Chem. Jpn.*, **44**, 806 (1986).
11. K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *J. Am. Chem. Soc.*, **113**, 4576 (1991).
12. K. Takahashi and T. Sakai, unpublished work.
13. K. Takahashi, A. Gunji, M. Yoshifuji, K. Akiyama, Y. Ikegami, unpublished work.
14. K. Takahashi and M. Ogiyama, *Tetrahedron Lett.*, **32**, 3507 (1991).
15. R. West and D. Zecher, *J. Am. Chem. Soc.*, **92**, 155 (1970); K. Komatsu and R. West, *J. Chem. Soc., Chem. Commun.*, 570 (1976).
16. K. Nakasuji, K. Yoshida, and I. Murata, *J. Am. Chem. Soc.*, **104**, 1432 (1982); **105**, 5136 (1983).
17. Y. Yamashita, S. Tanaka, K. Imaeda, and H. Inokuchi, *Chem. Lett.*, 1213 (1991); M. A. Coffin, M. R. Bryce, and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 401 (1992).
18. K. Takahashi and T. Suzuki, *J. Am. Chem. Soc.*, **111**, 5483 (1989).
19. K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **17**, 875 (1978).
20. K. Takahashi and M. Ogiyama, *J. Chem. Soc., Chem. Commun.*, 1196 (1990).
21. K. Takahashi, T. Nihira, K. Takase, and K. Shibata, *Tetrahedron Lett.*, **30**, 2091 (1989).
22. Y. Ueno, A. Nakayama, and M. Okawara, *J. Chem. Soc., Chem. Commun.*, 74 (1978).
23. K. Takahashi and T. Nihira, unpublished works.
24. K. Takahashi and T. Nihira, *Tetrahedron Lett.*, **30**, 5903 (1989).
25. M. R. Bryce and A. J. Moore, *Tetrahedron Lett.*, **29**, 1075 (1988).
26. Y. Ueno, M. Bahry, and M. Okawara, *Tetrahedron Lett.*, 4607 (1977).
27. M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1675 (1985).
28. S. Hünig and H. Berneth, *Top. Curr. Chem.*, **92**, 1 (1980).
29. C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, **10**, 49 (1981); T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, **55**, 4127 (1990).
30. S. Woitellier, J. P. Launay, and C. W. Spangler, *Inorg. Chem.*, **28**, 758 (1989); J. E. Sutton and H. Taube, *Inorg. Chem.*, **20**, 3125 (1981); Y. Kim and C. M. Lieber, *Inorg. Chem.*, **28**, 3990 (1989).
31. T. S. Arrhenius, M. B.-Desce, M. Dvolaitzky, J.-M. Lehn, and S. Kugimiya, T. Lazrak, M. B.-Desce, and J.-M. Lhen, *J. Chem. Soc., Chem. Commun.*, 1179 (1991).
32. K. Takahashi, T. Nihira, K. Akiyama, Y. Ikegami, and E. Fukuyo, *J. Chem. Soc., Chem. Commun.*, 620 (1992); K. Takahashi and T. Nihira, *Bull. Chem. Soc. Jpn.*, **65**, 1855 (1992).
33. K. H. Drexhage, G. R. Erikson, G. H. Hawks, and G. A. Reynolds, *Opt. Commun.*, **15**, 399 (1975); L. A. Lee and R. A. Robb, *IEE J. Quantum Electron.*, **16**, 777 (1980).