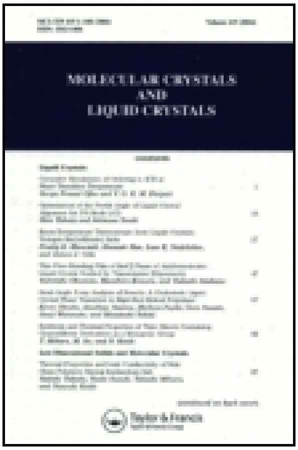

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Photoelectrochemical Spin Manipulation of N-Arylviologen Conjugated Molecules

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Photoelectrochemical Spin Manipulation of N-Arylviologen Conjugated Molecules

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N-arylviologen conjugated molecules, 4,6-bis(1'-methyl-4,4'-bipyridine-1-yl)-pyrimidine (**1**) and 3,6-bis(1'-methyl-4,4'-bipyridine-1-yl)-pyridazine (**2**) were designed and synthesized. Electrochemical, spectroscopic, and magnetic properties of such molecules were investigated. Their multi-step reduction processes involving ion-radicals generation were observed in both electrochemical and photochemical conditions. An attached electron in one electron reduced state, $\mathbf{2}^{3+}$, was more delocalized over the whole molecule than the case of $\mathbf{1}^{3+}$. The two electron reduced species, $\mathbf{1}^{2+}$, showed the ground state triplet biradical character, while $\mathbf{2}^{2+}$ had the quinoid-type closed shell structure. These features of electronic structure result from the natures of the heteroaromatic π-conjugated linkers used here.

Keywords: spin manipulation; conjugated assembly; N-arylviologen

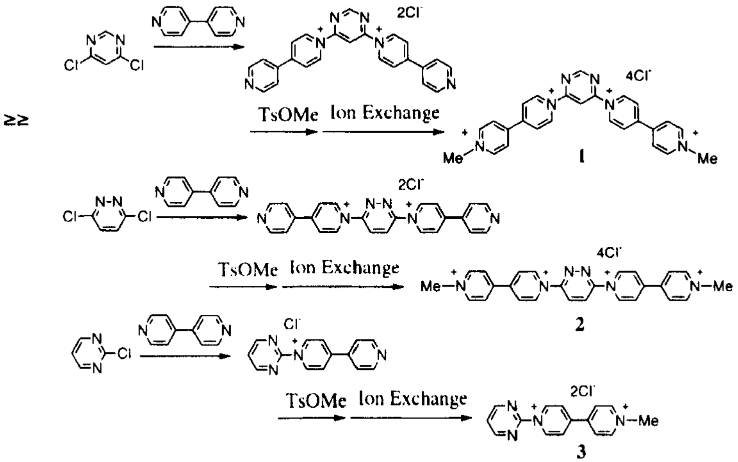
INTRODUCTION

Construction of nanometer-size object from simple molecules is one of the current topics in materials sciences[1]. There are various types of supramolecular systems, consisting of a variety of molecular components. Integration of electrochemically active components into such supramolecular system is a key process to demonstrate its whole properties, because the interaction between the neighboring components would produce novel multi-functions specific to the assembled structure. Viologens have been used as both electron acceptors and photo- or electrochromic molecules[2]. When plural viologen units are connected through appropriate π-conjugated linkers, the electrochemically or photochemically multi-electron reduced species of the conjugated viologen assemblies would involve several high-spin states with considerable spin exchange interaction. Along this line, we designed N-arylviologen conjugated molecules to elucidate the electronic interaction between the individual one-electron reduced ion-radicals. The present dimer molecules will provide significant knowledge to be extended to this kind of π-conjugated assembling of photochemically tunable ion-radical components.

RESULTS AND DISCUSSION

Design and preparation of N-arylviologens

Much different from alkylhalides, arylhalides resist nucleophilic substitution for pyridine. There have been several unusual examples on the nucleophilic substitution of halogeno-heterocyclic aromatic compounds, which should be suitable π-linkers in this study[3]. We designed 4,6-bis(1'-methyl-4,4'-bipyridine-1-yl)-pyrimidine (**1**) and 3,6-bis(1'-methyl-4,4'-bipyridine-1-yl)-pyridazine (**2**), using meta- and para-type heteroaromatic linkers, respectively, in analogy with the phenylene-linked biradicals. The designed *N*-arylviologens were prepared as described in Scheme 1. The viologen-type dimers were



SCHEME 1 Synthetic routes to N-arylviologen conjugated molecules

prepared from 4,4'-bipyridine and 4,6-dichloropyrimidine or 3,6-dichlropyridazine to give pyridinium-type dimer, followed by methylation with methyl-*p*-toluenesulfonate. Pyrimidine-2-yl-type monomer (**3**) was also prepared as a reference molecule.

Electrochemical properties of N-arylviologens

Electrochemical properties of the viologens were investigated by cyclic voltammetry and differential pulse voltammetry. The reduction waves of **1** and **2** were cathodically shifted with considerable splits in comparison with those of **3** as shown in Figure 1. The magnitude of the splits were 75 and 55 mV for **1** and **2**, respectively. These voltammograms suggest that the electronic states of two viologens interact each other through 4,6-pyrimidinylene and 3,6-pyridazinylene linkers. The reason why the redox potentials of **1** and **2** shift cathodically with respect to those of **3** may be explained here by the electron deficient properties of the N-substituents of the viologen moieties. Actually, the ^{1}H-NMR chemical shifts of the 2-protons of the pyridinium linked to the heteroaromatic linker were 10.08, 10.01 and 10.31 ppm for **1**, **2** and **3**, respectively. This results indicates that the 4,6-pyrimidinylene linker in **1** and the 3,6-pyridazinylene linker in **2** should have less positive inductive effect to the substituted viologen than the pyrimidine-2-yl substituent in **3**.

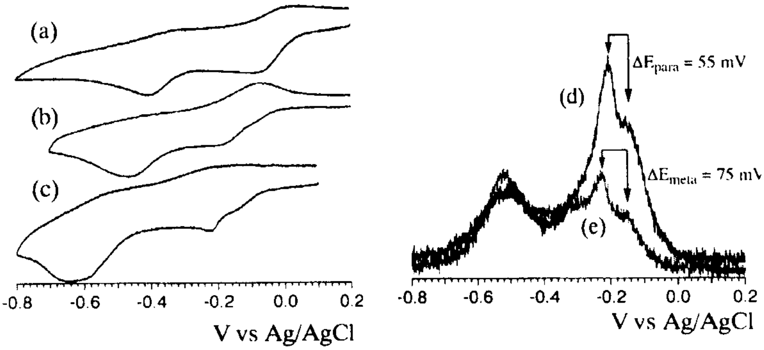


FIGURE 1 Cyclic voltammograms of the π-conjugated viologen assemblies **3** (a), **2** (b), and **1**(c) and differential pulse voltammograms of **2** (d) and **1** (e) in acetonitrile containing 0.1M *n*-Bu_4NBF_4

The reduction processes of **1** and **2** were also monitored by visible absorption spectroscopy on the electrolysis. At -0.20 V vs SCE of electrode potential, two broad absorption bands around 650 nm and 420 nm were observed in both dimers, similar to the one-electron reduced product of **3** ($\mathbf{3}^{+\bullet}$). These broad bands are assignable to ion-radical species. The considerable red-shift in $\mathbf{2}^{3+}$ in comparison with $\mathbf{1}^{3+}$ suggests that an attached electron on $\mathbf{2}^{3+}$ was more delocalized over the whole molecule than the case of $\mathbf{1}^{3+}$. The spectral difference between **1** and **2** was distinguished especially on the two-electron reduced species, $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively. While $\mathbf{1}^{2+}$ showed a broad band around 650 nm similar to the one-electron reduced products, the spectrum of $\mathbf{2}^{2+}$ lost the band characteristic of the ion-radical, similar to that of two-electron reduced viologen monomer $\mathbf{3}^{0}$. This result suggests that $\mathbf{1}^{2+}$ should be biradical, whereas $\mathbf{2}^{2+}$ has closed-shell quinoid structure as shown in Scheme 2.

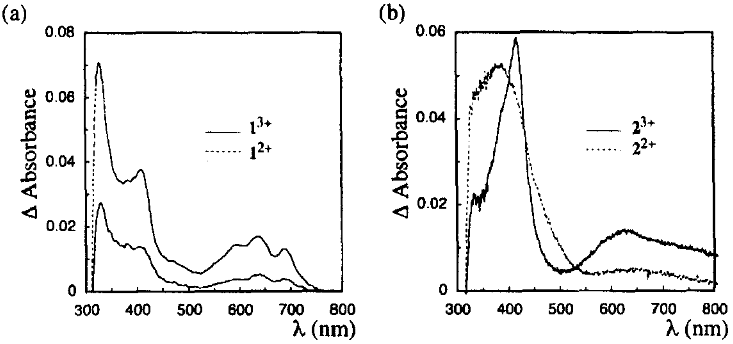
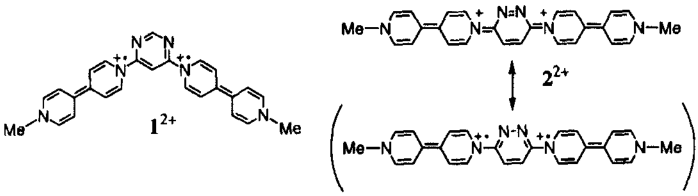


FIGURE 2 UV-Vis absorption spectra of electrochemically reduced species of **1** (a) and **2** (b) in acetonitrile containing 0.1M n-Bu_4NClO_4.



SCHEME 2 Structures for two-electron reduced products of **1** and **2**

ESR spectrum of meta-substituted viologen biradical

According to the absorption spectra, the two-electron reduced product, 1^{2+}, was identified to be biradical. The intramolecular spin-exchange interaction could be evaluated by low temperature ESR technique. The biradical was prepared by chemical reduction with zinc powder in acetonitrile solution. The ESR spectrum of 1^{2+} in a frozen matrix of acetonitrile at 10 K showed a set of signals with a fine structure and a half field band due to the triplet species as shown in Fig 3. Zero-field splitting parameters and anisotropic g values of the triplet species were determined to be $|D/hc| = 0.0205\ cm^{-1}$, $|E/hc| = 0.0017\ cm^{-1}$, $g_x = 2.0060$, $g_y = 2.0035$, and $g_z = 2.0023$, respectively

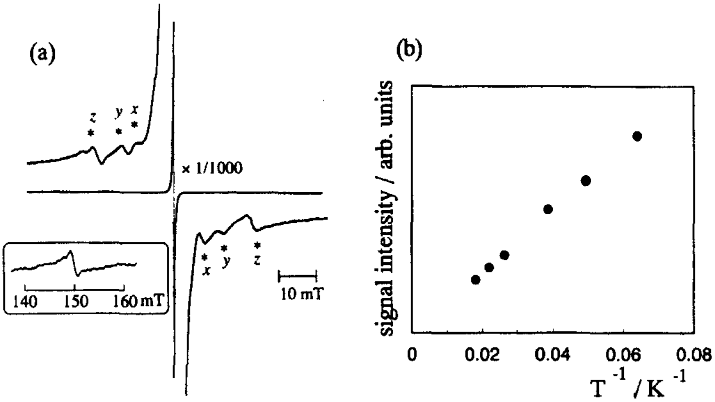
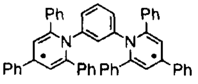


FIGURE 3 (a) ESR spectra of 1^{2+} in acetonitrile at 10 K. (b) Temperature dependence of the ESR signal intensities of the peak at half field region.

The triplet signal intensity increased in inverse proportion to temperatures, indicating that the triplet state should be the ground state of 1^{2+}. The singlet-triplet energy gap is estimated to be lager than 100 K. Okada *et al.* reported pyridinyl biradicals connected by phenylene linkers (**4** and **5**). Their spin-exchange interaction and D values are considerably smaller than that of 1^{2+}[4]. These pyridinyl biradicals have a twisted structure between the planes of the ion-radicals and the π-linker because of steric hindrance between the phenyl groups, to stabilize the ion-radical, and hydrogen atoms on the phenylene linker. Therefore, the intramolecular interaction through the π-linker and their D values should be smaller, because the two SOMOs of the biradical are localized on individual pyridinyl groups. On the other hand, **1** has pyrimidinylene linkers to reduce the steric hindrance between the viologen and the linker. These features are favorable to keep coplanality of the two viologen units and the pyrimidinylene linker, which brings larger spin-exchange interaction and D value.



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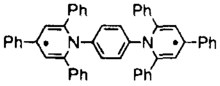

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Photoelectrochemical spin generation of the N-arylviologens

The ion-radical generation can be also demonstrated under light irradiation of **1** and **2**. The **1** and **2** films were prepared by casting from their polyvinylalcohol aqueous solution. UV irradiation of the films was carried out with a high-pressure mercury lamp through a pyrex filter (>300 nm) in the ESR cavity at room temperature. The ESR signal intensities of **1** monotonously increased

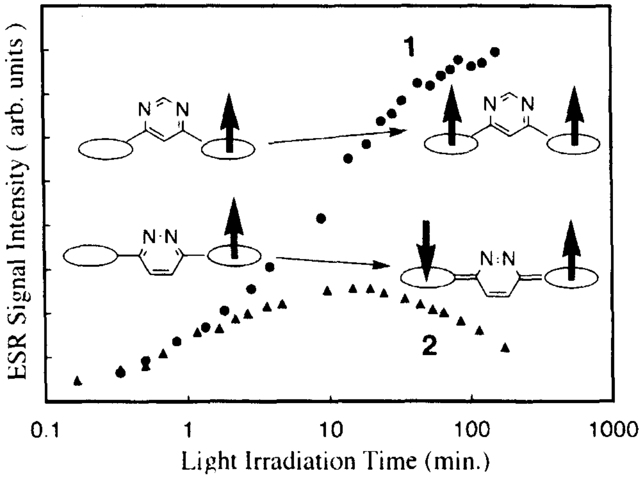
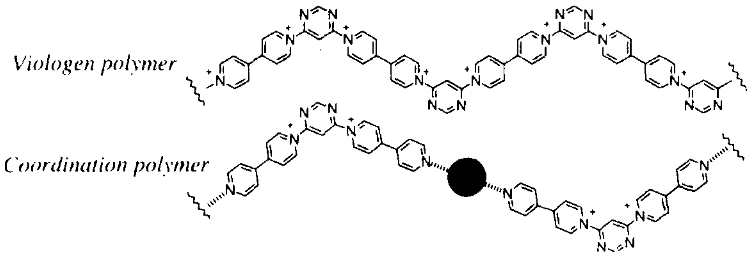


FIGURE 4 Photochemical spin generation on **1** and **2** in polyvinylalcohol matrix.

with irradiation time. On the contrary, the ESR intensity of **2** increased in the primary stage, and then it was saturated, followed by a gradual decrease with time. This result is interpreted as follows: In progress on the photochemical reduction process, at first, both **1** and **2** were one-electron reduced to generate their ion-radicals. Successive light irradiation would produce two-electron reduced species. Biradical $\mathbf{1}^{2+}$ continued to increase the signal, while quinoid-type closed-shell $\mathbf{2}^{2+}$ become silent in ESR. Therefore the signal intensity of **1** went on increase whereas **2** changed into decrease. These photochemical reduction processes mentioned above are consistent with the data of absorption spectra and ESR spectra of electrochemically reduced species.

CONCLUSION

Bifunctionalized N-arylviologens, 4,6-bis(1'-methyl-4,4'-bipyridine-1-yl)-pyrimidine (**1**) and 3,6-bis(1'-methyl-4,4'-bipyrdine-1-yl)-pyridazine (**2**) were synthesized. They exhibited clear differences in electronic structures of their ion-radical species depending on the π-linkers. Especially in meta-type dimer **1**, ground state triplet biradical was generated by both electrochemical and photochemical procedures. Although such photo-generated high-spin molecules have been well studied on polycarben molecules, they can only exist in considerably low temperature and with very short lifetime[5]. While the carben is generated irreversibly, $\mathbf{1}^{2+}$ is stable even at room temperature and can reversibly go back to the original state. They may be regarded as a prototype dimers to understand spin exchange interaction. Detailed study on extensive assembling of these dimer components into polymers by successive coupling or coordination with metal ions[6] is in progress, which will open a new avenue to realize interesting photo-electro-magnetic behaviors[7] specific to the assembling structure.



Acknowledgments

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