

Redox-tunable pyridinium assemblies and their interactive spin-based functions*

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Abstract: A new concept of conjugated functional assembly is proposed, leading to a guideline for function-directed supramolecules [1] and molecular systems [2] in which the functional building units are self-assembled with considerable interactions among them and the whole functions more than simple sum of the functions of the constituent blocks may be expected. The multi-mode chemical transducer is summarized, leading to the above concept. Photoelectrochemical spin-based function is introduced as the prototype of conjugated functional assembly.

INTRODUCTION

Dyes and pigments have been investigated for a long time. One significant motivation is to design new dyes and pigments for industrial requirement, and the other is to understand their electronic transition as a suitable model for π -conjugated systems. In last two decades, the color chemistry has grown, merging photographic chemistry and widely including electroluminescent materials, non-linear optical materials, π -conjugated systems, various chromisms such as photochromism and electrochromism, photoresist materials, and so on. Another significant approach is the application of the characteristic electronic states to advanced materials science. The target in this paper is photoelectrochemical spin manipulation of viologen conjugated functional assemblies to understand spin-spin interaction mediated by the intervening conjugated path and to establish a guideline for tunable magnetic materials.

CONCEPT OF CONJUGATED FUNCTIONAL ASSEMBLIES

A number of photochromic molecules have been known exhibiting two distinct electronic states which are thermally stable due to appreciable activation energy between the states but can be converted each other through the respective photoexcited states. In other words, the photochromism is described as one of the typical functions responsive to external stimuli, which has attained a significant position as a functional element in the field of molecular electronic devices [3]. Electrochromism, another leader of the well-known responsive functions, is exhibited on the basis of that either reduction or oxidation process should largely change the electronic states. Up to date numerous studies on both chromic properties have been focussing absorption spectral changes in visible light region, as materials for color chemistry. However, emphasis should be taken on considerable changes of electronic states during the chromic processes, i.e. not only the absorption spectral change but also any changes in optical, electric, and magnetic properties, all of which may have potential to be utilized as elemental responses for function-directed supramolecules.

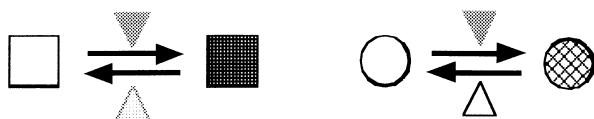
Scheme 1 describes the responsive interconversion processes by using two types of minimal conjugated functional assemblies. The states of elementary responsive blocks are controlled reversibly by external stimuli. There are two ways to link two responsive blocks through π -conjugated path, which has

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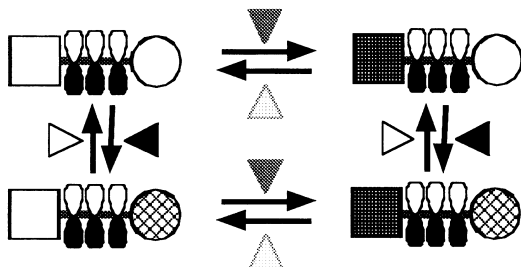
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potential to mediate electronic interaction between the blocks. One is hetero-conjugated assembly consisting of plural independent responsive blocks, called multi-mode chemical transducer mentioned in our previous reports [4–7]. The assembly in case of (B) has four distinct states and includes two responsive modes, as will be described in the next section. The other is homo-conjugated assembly consisting of plural identical blocks, which is demonstrated by two viologen conjugated dimers. The interconversion in case of (C) involves two-step successive processes controlled by the identical stimulus. Although the latter sounds more primitive than the former, but there still remain several questions to be solved for the function-directed supramolecules and molecular systems. For example, two kinds of the intermediate states should be considered in the successive processes. One is the ‘localized state’ in which the responded state is localized at one block of the assembly, and the other is the ‘delocalized state’ in which the responded state is delocalized over the assembly.

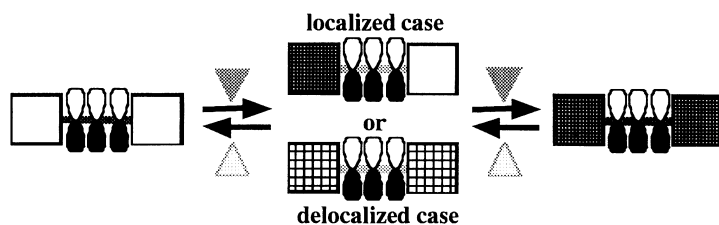
(A) Single responsive molecule



(B) Hetero-conjugated responsive molecule



(C) Homo-conjugated responsive molecule

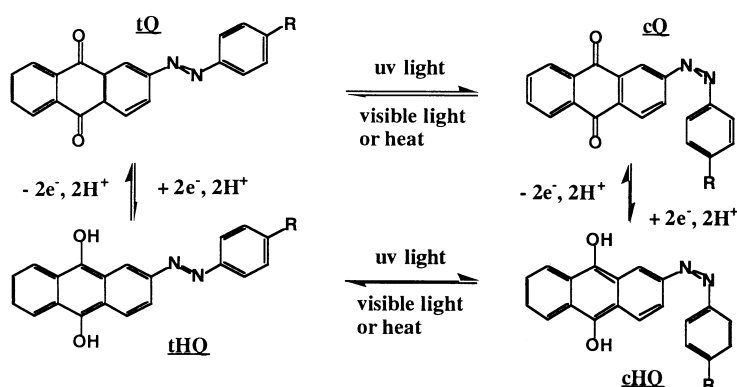


Scheme 1 Interconversion processes of the conjugated functional assemblies of responsive blocks (squares and circles). Triangles at arrows are external stimuli. (B) Four distinct states are controlled by two kinds of stimuli, called multi-mode chemical transducer. (C) Two-step process is controlled by successive stimuli. Two kinds of intermediate state may be considered, i.e. the responded site is localized at one block or delocalized over the molecule.

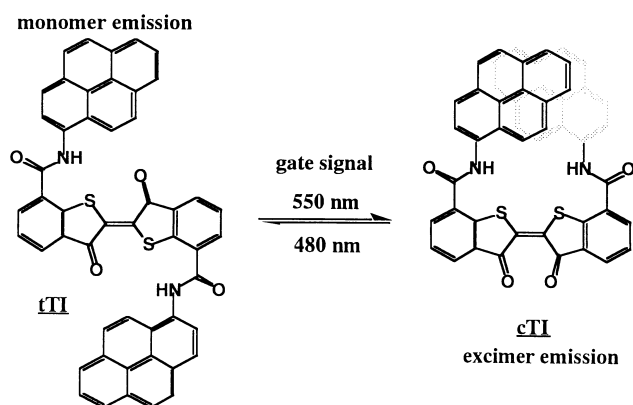
MULTI-MODE CHEMICAL TRANSDUCER

Let us link two responsive building blocks with considerable interaction as the smallest conjugated functional assembly. One of the authors (T.I.) have already demonstrated the conjugated functions by synthesizing several azo-quinone compounds which have fused structure between photochromic azobenzene and electrochromic quinone moieties [4]. This molecule, to our best knowledge, was the first example to interactively combine photochromism and electrochromism. As Scheme 2 shows, the azo-quinone compound shows four distinct states, **tQ**, **cQ**, **thQ**, and **chQ**, resulted from isomerization process of the azobenzene moiety and two electron reduction process of the quinone-hydroquinone moiety. Interestingly, thermal isomerization from **cQ** to **tQ** undergoes 30 times more quickly than that from **chQ** to **thQ**. Suppose this molecule is regarded as both photochromic and electrochromic molecular memory, the thermal stability of two cis-forms, **cQ** and **chQ**, resulted from photoisomerization can be changed by redox states of the quinone-hydroquinone moiety: The **cQ** is a ‘shallow’ memory

state to be easily converted to **tQ**, while **cHQ** is a 'deep' memory state to be kept more permanently. This demonstration can lead to a more generalized concept. (i) The molecule has multiple functional moieties responsive independently to the stimuli. (ii) These moieties have considerable interactions through the conjugated path between them. Consequently, a molecule with **n** responsive moieties would have 2^n states corresponding to **n** interconversion processes for every independent stimulus. Also, all the interconversion modes would be dependent each other. The independent signal interconversions are termed as conjugated functions which is just a center of this paper. Saika *et al.* extended the multi-mode chemical transducer to demonstrate monomer-excimer emission control of two pyrenyl substituents of which intramolecular arrangement can be varied by the photoisomerization of the parent thioindigo groups [5]. Under photoexcitation at 340 nm, two pyrenyl groups in **cIT** may take partly overlapped conformation to exhibit the intramolecular excimer fluorescence, while those in **tIT** show monomer fluorescence, as Scheme 3 shows. The monomer and excimer fluorescences can be, therefore, controlled by the reversible photoisomerization between **tIT** and **cIT** under photoirradiations at 550 nm and 480 nm as a gate signal of this optical switching system. Further extended study has been carried out by switching of the π -conjugated path between the oligothieryl groups at both wings through reversible photoisomerization of the diarylethene derivatives.



Scheme 2 Multi-mode chemical transducer of azo-quinone compound.



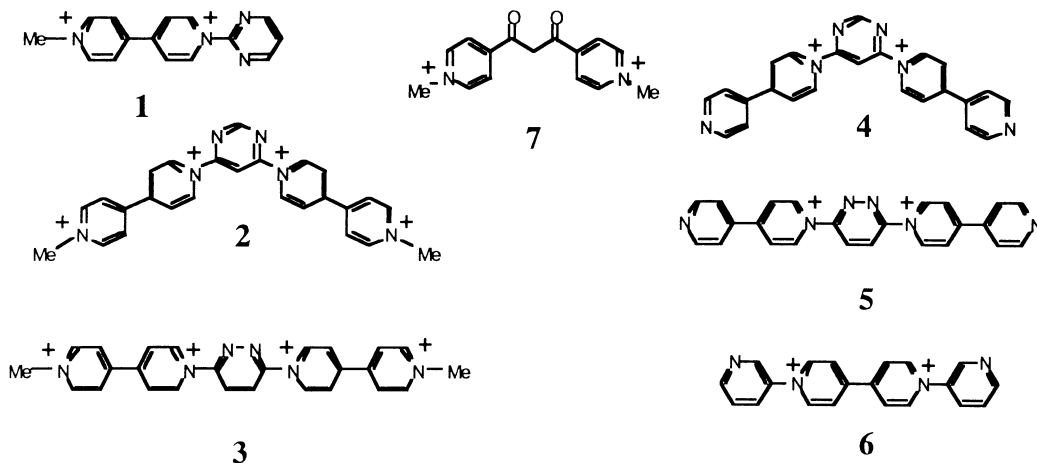
Scheme 3 Multi-mode chemical transducer of pyrenyl-substituted thioindigo.

VIOLOGEN AND PYRIDINIUM CONJUGATED ASSEMBLY [8]

Viologen is a well-known molecule as an electron acceptor to mediate a photo-induced electron transfer sequence and to be paired with various electron donors in charge transfer complexes as well as an electrochromic molecule based on strong coloration of its one-electron reduced state. The reversible two-step redox process involving dication, monocation radical, and neutral quinoid has been established. The

paramagnetic monocation radical has an unpaired electron in π^* orbital and can be also generated through photo-induced electron transfer from the counter anions such as bromide and iodide ions or the surrounding media such as alcohol.

In this project we have chosen the viologen and its relating molecules as a core molecule of the spin-based functional blocks, as Scheme 4 shows. The viologen dimers, **2** and **3**, were synthesized so as to demonstrate the four-step redox processes and to understand spin-spin interaction of the two attached electrons, which provided significant nature of the heteroaromatic linkers between two viologens, 4,6-pyrimidinylene and 3,6-pyridazinylene. The pyridylpyridinium dimers, **4** and **5**, have two redox-tunable pyridinium moieties as well as two pyridyl groups acting as coordination sites. The viologen **6** has two 3-pyridyl groups with enough basicity to coordinate metal ion, based on meta orientation from the electron withdrawing viologen bridge. These redox-tunable ligands were designed for coordination self-assembling with various metal ions and metal complexes. The β -diketone ligand **7** having two pyridinium groups was designed for various kinds of metal complexes, in which both intra- and inter-ligand spin exchange interactions may be examined and the d- π interaction would influence these electronic interactive paths. Additionally, the replacement of methyl groups on nitrogen of the pyridyl moieties by appropriate long alkyl groups allows the molecule to be amphiphilic to give discotic liquid crystalline with π - π stacking effect.

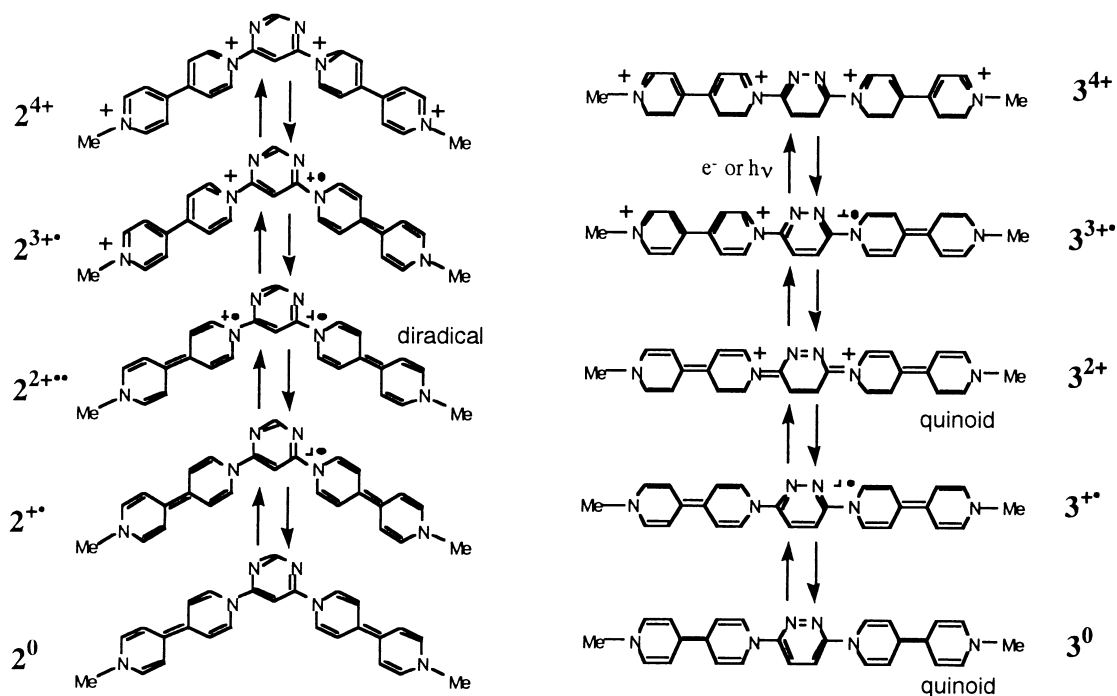


Scheme 4 The redox-tunable functional building blocks.

PHOTOELECTROCHEMICALLY TUNABLE VIOLOGEN DIMERS [9]

Scheme 5 shows the four-step redox processes of the viologen dimers, which was conclusively obtained by cyclic voltammetry, differential pulse voltammetry, UV-vis absorption spectra under potentiostatic condition, and cryogenic esr spectra of the two-electron reduced state, as follows.

Two reduction waves of **1** are observed at -130 mV and -490 mV vs. Ag/AgCl in acetonitrile containing 0.1 mol/L tetrabutylammonium perchlorate (TBAP), in which both are assigned to successive reduction processes to monocation radical and then neutral quinoid. Each wave are shifted anodically and split into two as shoulders by about 70 mV in both dimers **2** and **3**. These split waves suggest that the electronic states of two viologens interact each other through 4,6-pyrimidinylene and 3,6-pyridazinylene linkers. These four-step reduction processes of **2** and **3** were also demonstrated by visible absorption spectroscopy under potentiostatic condition. At -200 mV vs Ag/AgCl of electrode potential as the first reduction process, two broad absorption bands around 650 nm and 420 nm were observed in both dimers, similar to the one-electron reduced product $\mathbf{1}^+$. Considerable red-shifted and tailed visible band in $\mathbf{3}^{3+}$ in comparison with $\mathbf{2}^{3+}$ suggests that an attached electron on $\mathbf{3}^{3+}$ was more delocalized over the whole molecule than the case of $\mathbf{3}^{3+}$. Striking contrast was found in the spectra of two-electron reduced states of both dimers. While the broad absorption band around 650 nm continued to grow in the second process of **2**, the corresponding red-shifted band disappeared in case of $\mathbf{3}^{2+}$, similar to that of fully reduced viologen monomer $\mathbf{1}^0$.



Scheme 5 The four-step reduction processes of the viologen dimers

The cryogenic esr spectra of 2^{2+} , prepared by chemical reduction with zinc powder, showed triplet signal with strong doublet and a half field band, while 3^{2+} gave no ESR signal. Zero-field splitting parameters and anisotropic g values of the triplet species 2^{2+} were determined to be $|D/hc| = 0.0205 \text{ cm}^{-1}$, $|E/hc| = 0.0017 \text{ cm}^{-1}$, $g_x = 2.0060$, $g_y = 2.0035$, and $g_z = 2.0023$, respectively. A linear relationship between triplet signal intensity and reciprocal temperature indicates that 2^{2+} should be triplet diradical in the ground state with at least higher than 100 K of singlet-triplet energy gap. On the contrary, 3^{2+} has closed-shell quinoid structure. In the third reduction of **2** the 650-nm absorption decreased by a factor of 2, and finally disappeared after the fourth reduction, implying that one of viologen units in 2^+ should be mono-ion radical and the other should have neutral quinoid structure. The 650-nm absorption band reappeared and disappeared in the third and the fourth reduction processes of **3**, respectively.

Interestingly, these four-step reduction processes of the dimers could be demonstrated successively in time when their methanol solutions were irradiated by UV light through a Pyrex filter ($>300 \text{ nm}$). These photochemical processes would take place step by step via photo-induced successive electron transfer from their counter anion or the surrounding methanol molecules. In conclusion, the four-step reduction processes can be conducted both electrochemically and photochemically, and the 4,6-pyrimidinylene linker plays a significant role in mediating considerable ferromagnetic interaction between the neighboring spins on the viologen wings.

The ion-radical generation can be also demonstrated under light irradiation of **2** and **3**. The **2** and **3** 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 ($>300 \text{ nm}$) in the ESR cavity at room temperature. The ESR signal intensities of **2** monotonously increased with irradiation time. On the contrary, the ESR intensity of **3** 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 **2** and **3** were one-electron reduced to generate their ion-radicals. Successive light irradiation would produce two-electron reduced species. Biradical 2^{2+} continued to increase the signal, while quinoid-type closed-shell 3^{2+} become silent in ESR. Therefore the signal intensity of **2** went on increase whereas **3** changed into decrease. These photochemical reduction processes mentioned above are consistent with the data of absorption spectra and ESR spectra of electrochemically reduced species.

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REFERENCES

- 1 J. M. Lehn, J. L. Atwood, J. E. D. Davies, ed. *Comprehensive Supramolecular Chemistry*. Pergamon, UK (1995).
- 2 K. Honda, ed. *Functionality of Molecular Systems*. Vol. 2, *From Molecular Systems to Molecular Devices*. Springer-Verlag, Tokyo (1999).
- 3 F. L. Carter. *Molecular Electronic Devices*. Marcel Dekker Inc., New York (1982).
- 4 T. Iyoda, T. Saika, T. Shimidzu, K. Honda. *Tetrahedron Lett.* **30**, 5429 (1989).
- 5 T. Saika, T. Shimidzu. *J. Chem. Soc. Chem. Commun.* 951 (1992).
- 6 T. Saika, T. Iyoda, T. Shimidzu. *J. Chem. Soc. Perkin Trans.* **2**, 1181 (1993).
- 7 T. Saika, T. Iyoda, K. Honda, T. Shimidzu. *Mol. Cryst. Liq. Cryst. Technol. Sect A*, **246**, 319 (1994).
- 8 T. Iyoda, M. M. Matsushita, M. Morikawa, T. Kawai. *Macromol. Symp.*, in press.
- 9 M. M. Matsuhita, T. Tachikawa, T. Suzuki, T. Kawai, T. Iyoda. *Mol. Cryst. Liq. Cryst.* **334**, 149 (1999).