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Tunable Molecular Magnetism in Conjugated Assembly of Functional Spin Units

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SUMMARY: Molecular design and photoelectrochemically responsive functions of several redox-tunable building blocks toward conjugated assembling were described. The viologen dimers and pyridylpyridinium dimers through π-conjugated linkers showed multi-step redox processes which were demonstrated electrochemically and photochemically. The 4,6-pyrimidinylene and 3,6-pyridazinylene linkers played an important role as effective mediators between two attached electrons in the two viologens or pyridinium groups. The latter pyridylpyridinium dimers and 3-pyridylviologen have potential to coordinate various metal ions to give conjugated self-assemblies.

Introduction

Remarkable progress has been made in the field of molecule-based magnetism, since the first demonstration of magnetic phase transition of organic radical crystals[1)] and polymeric metal complexes[2)] at very low temperature. There have been synthesized more than decades of molecules showing the macroscopic spin ordering last ten years. While the Curie temperatures of the magnetic phase transitions of purely organic magnets still stay around a few K, those of well-characterized metal complex magnets have been elevated up to room temperature, and finally the Curie temperature higher than 400 K was achieved in polymeric metal complexes of $V(TCNE)_x$[3)]. Another movement in this field was bone in 1996, to control the magnetic properties by external stimuli, i.e., an attached or removed electron, light irradiation, counter ion exchange towards the parent ionic complexes, and so on. Hashimoto and his group first demonstrated the electrochemical control of the Curie temperature of chromium cyanide polymeric complex, Prussian blue analogue, in the range of 80-260 K by tuning the valence of the chromium ions[4)]. Their most successful demonstration along the stimulus-responsive molecule-based magnet was to reversibly control the macroscopic magnetic phases between paramagnetism and ferrimagnetism in the polymeric cobalt iron cyanide complexes[5)]. Energetically almost degenerate states between Fe^{2+}-CN-Co^{3+} and Fe^{3+}-CN-Co^{2+} should be essential to convert between two magnetic phases through the photo-induced metal-to-metal electron transfer. Additional feature is spin

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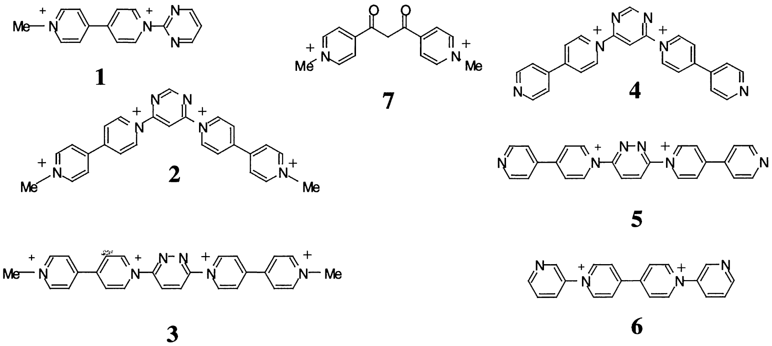
crossover process on cobalt ion, in which Co^{2+} tends to have high-spin state. Since these findings we have set our motivation to extend the concept of the tunable molecular magnetism, not only to search other tunable molecule-based magnets but also to understand the electronic interaction between spins on building blocks in a molecular assembly, which is rapidly growing in view of supramolecular chemistry. Molecular magnetism is one of the best probes to elucidate the magnitude and paths of electronic interaction in a designed self-assemblies consisting of spin-based functional building blocks. This information is promised to provide a significant guideline to manipulate electronic states of the assembly structure, directly leading to the specific electric, magnetic, and photonic functions. The time has come, the authors do think, that the next target in this field should be extended over by intentionally integrating other functions. One of the targeted functions is the "photoelectrochemical tuning of spin-based materials". Along this line we are describing our recent progress in a new type of molecular assemblies consisting of valence-tunable building blocks, directing to the spin-based functional materials.



Scheme 1: The redox-tunable functional building blocks

Molecular Design of Tunable Spin Blocks

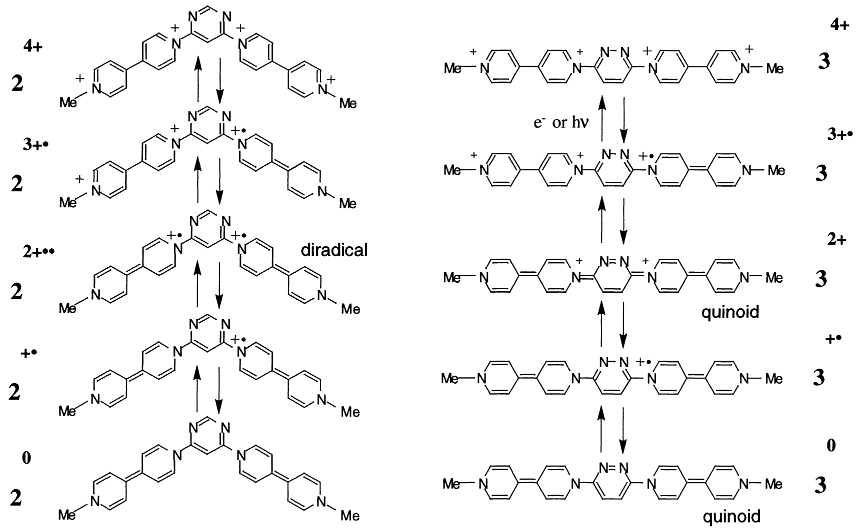
Viologen is a well-known molecule as an electron acceptor to mediate a photo-induced electron transfer sequence and to be paired with various electron donors in charge transfer complexes as well as an electrochromic molecule based on strong coloration of its one-electron reduced state⁶⁾. The reversible 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 reducible 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 1 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-pyridadinylene. 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. 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.

Viologen Dimers

Scheme 2 shows the four-step redox processes7) 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 **1** and **2** 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 **2**$^{3+}$ in comparison with **3**$^{3+}$ suggests that an attached electron on **2**$^{3+}$ was more delocalized over the whole molecule than the case of **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 **3**, the corresponding red-shifted band disappeared in case of **2**$^{2+}$, similar to that of fully reduced viologen monomer **3**^{0}.



Scheme 2: The four-step reduction processes of the viologen dimers.

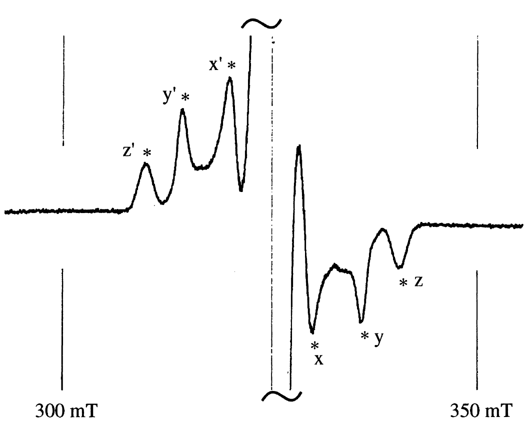


Figure 1 ESR spectrum of 22+ in DMF at 14 K

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 $|D/hc| = 0.0205\ \mathrm{cm}^{-1}$, $|E/hc| = 0.0017\ \mathrm{cm}^{-1}$, $g_x = 2.0060$, $g_y = 2.0035$, 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 re-appeared 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 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.

Redox-tunable Ligands

A couple of reduction waves were observed at –257 mV and –422 mV vs. Ag/AgCl in acetonitrile containing 0.1 mol/l TBAP for **4**, -336 mV and 499 mV for **5**, and –61 mV and –350 mV for **6**, respectively, based on their differential pulse voltammograms. In a similar manner, the corresponding absorption spectral changes were observed under potentiostatic condition. The uv-visible absorption change during the reduction was consistent with those of methyl viologen and **1**. In both pyridylpyridinium dimers **4** and **5**, the 350-nm shoulder peaks assigned to pyridyl radical increased and the parent 300-nm π–π* bands decreased successively during the two-step reduction processes, completely different from the case of two-electron reduced states of the viologen dimers.

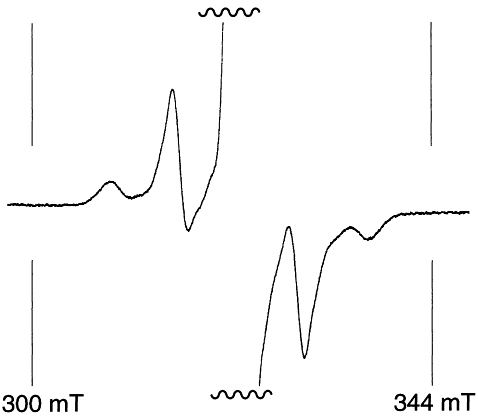


Figure 2 ESR spectrum of **5** in DMF at 13 K

That is to say, monotonous spectral change should be noticed even in the 3,6-pyridadinylene-linked dimer **5**, since a classical Kekure structure cannot be drawn in it. Figure 2 shows a triplet signal in esr spectrum of two-electron reduced state of **5**, which was prepared by uv irradiation in methanol glass at 13 K. The $|D/hc|$ values are 0.0132 cm^{-1} and $g = 2.0033$. The two-electron reduced state of **4** also showed triplet signal with $|D/hc| = 0.0133$ cm^{-1} and $g = 2.0033$. Slightly longer distance between the unpaired electrons than the case of the viologen dimer **2** was suggested. It was also concluded that these pyridylpyridinium dimers and 3-pyridylviologen should act as redox-tunable ligands as we designed. Table 1 summarizes the present result of the coordination polymers prepared by mixing these ligands with various metal ions and metal complexes. A detailed study on their structures and magnetic properties is in progress.

Table 1. The result of self-assembling of the redox-tunable spin units.

metal ion or metal complex	**4**	**5**	**6**
$Mn(NO_3)_2$	-	orange solid	-
$CoCl_2$	green solid	green crystal	yellow crystal
$Ni(NO_3)_2$	yellow powder	green solid	yellow crystal
$NiCl_2$	-	-	yellow crystal
$Cu(ClO_4)_2$	blue crystal	green solid	green solid
$Zn(ClO_4)_2$	-	brown solid	brown crystal
$PdCl_2$	white powder	pink powder	yellow powder
AgX ($X=NO_3^-$, BF_4^-)	white crystal	white solid	-
CdY_2 (Cl^-, I^-, NO_3^-)	-	yellow crystal	yellow solid
$Cu(hfacac)_2$	-	red crystal	brown crystal

Pyridyl-β-diketone Ligand

The β-diketone ligand conjugated with two pyridinium groups shows almost 100 % enol form and two-step redox process at –210 mV and –640 mV vs Ag/AgCl in DMF. The one- and two-electron reduced states exhibited 450-nm shoulder in uv-vis absorption spectra, characteristic of a pyridyl radical. Four- and six-step redox processes may be expected in its divalent and trivalent metal complexes, and both intra- and interligand interactions of plural pyridyl radicals through pseud-aromatic ring consisting of the metal ion will be evaluated.

Acknowledgments

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