Recent progress in the redox chemistry of multimetallic transition-metal complexes and clusters is reviewed. Special attention is paid to high-nuclearity complexes wherein redox-active sites (e.g., ferrocenyl pendants or Ru centers) are assembled in a close proximity with a well-defined geometry via the covalent or coordination bonds. A special emphasis is placed on literature survey for paddlewheel diruthenium(II,III) complexes coordinated by axial or equatorial ferrocenyl ligands, polyferrocenyl compounds in the form of wire, star, and ring, ferrocenyl-based dendrimers, and ligand-mediated molecular triangles and squares. Finally, future prospects of these mixed-valent systems are briefly discussed.

1. Mixed-Valent Compounds

Ligand-bridged mixed-valent binuclear complexes have played a vital role in coordination chemistry in their importance for understanding electron delocalization and metal-metal coupling through the bridging ligands. One of the best studied in this research field is so-called Creutz-Taube ion formulated as [(NH₃)_5Ru(μ-pz)Ru(NH₃)_5]⁺⁺ (pz = pyrazine) (Fig. 1).¹⁻³ This binuclear ruthenium complex is regarded as exhibiting Class III behavior in the Robin-Day classification,⁴ where the valence is fully delocalized over the two Ru centers through pz to give an averaged oxidation state Ru².⁵ Naturally, mixed-valence chemistry of many other derivatives of this complex have been exploited extensively to study effects of bridging ligands, ancillary ligands, and metal centers on the extent of valence delocalization.⁵⁻⁸

Metal-metal interactions can be conveniently examined by electrochemical methods. When two redox-active metal centers connected with a bridge and the two metal sites interact to each other, successive two one-electron transfer reactions occur with the separation of the respective half-wave potentials (E₁/₂(1) and E₁/₂(2)) in the cyclic voltammogram (CV), defined as ΔE₁/₂ = E₁/₂(1) − E₁/₂(2), in which the ΔE₁/₂ value is frequently taken as a measure for the extent of two-site interactions on molecules of interest (Eq. 1).

\[
\begin{align*}
M – L – M & \rightarrow M^+ – L – M \\
E_{1/2}(1) & \quad E_{1/2}(2)
\end{align*}
\]

Here, M = a redox-active metal site; M' = a one-electron-oxidized metal site; L = a bridging ligand. The thermodynamic stability of the mixed-valent state of the binuclear system can be accessed by comproportionation constant Kₐ(co) (Eqs. 2 and 3).⁹

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Fig. 1 Chemical structure of the Creutz-Taube ion.
mediating bridge (through metal centers, wherein the metal centers act as a version, structural variation and complexity have been synthesized reported in the last half a decade. Future prospects concerning electroactive sites, showing multiple numbers of the ground-state electron-tran... from M to M’ that may occur in the near infrared (NIR) region.

Due to stimulus interest in electroactive materials for studies on electron transfer, electrochemical sensing, and catalysis, together with potential application to electronic devices, redox-active transition-metal complexes with structural variation and complexity have been synthesized recently, including those containing more than two electroactive sites, showing multiple numbers of the ground-state electron-transfer and excited-state charge-transfer. This review article describes such recent development of chemistry of mixed-valent complexes with special emphasis on those reported in the last half a decade. Future prospects concerning with mixed-valent transition-metal chemistry, including some applications, is also discussed.

### 2. Mixed-Valency of Ferrocenyl Groups Attached to Dimetal Skeletons via Coordination.

Ferrocene and its derivatives have played a central role in coordination chemistry for electroactive materials. A particular attention has been paid recently to ferrocenyl compounds that are modified with pendant(s) showing coordination ability to transition-metal centers, such as ferrocenyl carboxylates. These ferrocenyl ligands are regarded as redox-active probe for the investigation of metal–metal communication when two (or more) are attached to metal or cluster centers of interest. The mixed-valent state for iron centers in ferrocenyl ligands formed during the oxidation process can be investigated by cyclic voltammetry and other electrochemical techniques including spectroelectrochemistry.

The ferrocenylethynyl moiety is particularly useful ligands for accessing charge mobility across mononuclear metal center (Ru) as well as dinuclear (Pt) and trinuclear (Cu) metal centers. A series of paddlewheel diruthenium complexes bearing two ferrocenyl groups in the axial positions have been prepared. The examples include trans-(FeC≡C)nRu2(Y-DMBA)(C=C)F (n, m = 1 and 2; Y-DMBA = N,N'-dimethylbenzamidinate or N,N'-dimethyl-(3-methoxy)benzamidinate; Fe = ferrocenyl group) (Fig. 2). Peak separations in the oxidation process were 0.31 and 0.30 V for compounds with Y = OCH3 and OC6H5, respectively, indicating an excellent ability of...
Not only for the axial positions, two Fc groups that are situated in the equatorial sites of the paddlewheel diruthenium core can also show mutual interactions. Paddlewheel diruthenium compounds Ru₂(D(3,5-Cl₂Ph)F)₄⁻n(O₂CFc)₂⁻Cl (D(3,5-Cl₂Ph)F = N,N'-di(3,5-dichlorophenyl)formamidinate; n = 1 or 2) and Ru₂(DmAniF)₄⁻n(O₂CFc)₂⁻Cl (DmAniF = N,N'-di(3-methoxyphenyl)formamidinate; n = 1 or 2) have been synthesized from carboxylate exchange reactions of Ru₂(D(3,5-Cl₂Ph)F)₄⁻n(OAc)₂⁻Cl and Ru₂(DmAniF)₄⁻n(OAc)₂⁻Cl, respectively (Scheme 2). Cyclic voltammetry reveals stepwise one-electron oxidation due to Fc moieties to form monocationic mixed-valent complexes which shows Class II behavior in the Robin-Day classification.

Carboxylate exchange reactions provide a series of paddlewheel dimetal complexes with four equatorially coordinated ferrocenylicarboxylate (fca) ligands. Examples that were structurally determined by X-ray crystallography include [Mo₂(μ-fca)₄(CH₃CN)(DMSO)]²⁺DMSO (DMSO = dimethylsulfoxide), (Cu₂(μ-fca)₄(THF))²⁺THF, and [Ru₂(μ-fca)₄(1-propanol)]PF₆. As a similar but more flexible system, diruthenium(II,III) compounds with equatorial Fc groups wherein a series of organic linkers is introduced between the Fe and carboxylate groups have been prepared and characterized. Electrochemistry on these compounds exhibited a diminished extent of the Fc–Fc coupling observed in [Ru₂(μ-fca)₄(1-propanol)]PF₆ when a single methylene spacer was introduced between the Fc group and the carboxylate group. When a conjugated linker, –CH=CH–, was introduced, a very small degree of mutual communication between the Fc groups was observed (the peak separation of 41 mV in 0.1 M n-Bu₄NPF₆–1,2-dichloroethane), suggesting a through-bond character of the Fc–Fc coupling despite of the metal–metal distance over 7 Å. In a linearly-arranged tricobalt complex with axial ferrocenyl pendants [Co₃(dpa)₄](dpa = 2,2'-dipyridylamide), so-called “extended metal atom chain (EMAC)”, the oxidation of the Fe moieties occurred nearly simultaneously with $K_c = 16$. Apart from the dinuclear skeletons, higher-nuclearity clusters are also good motifs that are able to mediate electronic communications between coordinated redox-active moieties. This transmitting ability may be even larger than that of mononuclear systems if long-range pathways for electronic coupling are prepared over the molecules by attaining efficient overlap of metal d- and ligand π- (or π*)-orbitals with a smaller energy gap between them. As seen in the above paragraphs, the coordination ability and reversible redox-activity of the ferrocenyl carboxylates provide a good opportunity to assess the extent of electronic coupling in shorter-to-longer scales via (multi)metallic centers of interest. The utilization of this interesting redox-active molecule will be further exploited in future to produce topologically and electronically interesting metal complexes by a judicious selection of substitution sites.

### 3. Electrochemistry and Mixed-Valency of Multiple Ferrocenylic Sites Covalently-Attached to Aromatics.

#### 3.1. Small Aromatics.

The mediation ability of thiophene and pyrrole moieties was examined by attaching four ferrocenyl moieties to the periphery of those molecular platforms; the compounds examined were 2,3,4,5-tetraferrocenyli thiophene and...
2,3,4,5-tetraferrocenyl-1-phenyl-1H-pyrrole\(^{35}\) (Fig. 3). Both compounds exhibit well-separated four one-electron reversible oxidation waves in CH\(_2\)Cl\(_2\) when \(n\)-Bu\(_4\)NB(C\(_6\)F\(_5\))\(_4\) was used as a supporting electrolyte. The electrolyte anion effect was significant in these systems. When \(n\)-Bu\(_4\)NPF\(_6\) was used as the supporting electrolyte, the pyrrole compound showed much reduced spread of the \(E_{1/2}\) and an extensive overlap of the first and second oxidation waves.

Fehlner and the co-workers examined redox processes of a tetranuclear square-shaped mixed-valent complex \([\text{Fc}_4(\eta^4-C_4)\text{CoCp}]\) (Fc = ferrocenyl, Cp = \(\eta^4\)-cyclopentadienyl anion) (Fig. 4) where electron transfer occurs intramolecularly.\(^{36,37}\) In CH\(_3\)CN/CH\(_2\)Cl\(_2\) mixed solvent system, this complex shows four redox waves associated with successive one-electron transfer (Fig. 5) where one-electron- and two-electron-oxidized, mixed-valent states are stable with \(K_{\text{com}} = 510\) and 346, respectively. The monocationic complex \([\text{Fc}_4(\eta^4-C_4)\text{CoCp}]\)PF\(_6\) was actually isolated and the structure was determined by X-ray crystallography. The Class II behavior of the monocationic complex was suggested by an appearance of solvent-dependent IVCT bands, and the valence was confirmed to be localized on the timescale of EPR, Mössbauer, and IR. A range of spectroscopic analysis and magnetic measurements revealed that the dicationic complex contains a two-electron and two-hole mixed-valence state. There are two possible redox isomers (cis and trans) for the two-electron-oxidized species but the trans geometry may be favored due to the electrostatic reason. The system is suggested to be appropriate for use in molecular quantum-dot cellular automata (QCA; see below).

### 3.2. Porphyrins

Free-base porphyrin core is also a good mediator for intramolecular electronic coupling. The synthesis, structural characterization, and electrochemistry for a series of free-base meso-poly(ferrocenyl)-containing porphyrins (Fig. 6) and their derivatives have been extensively studied.\(^{38-42}\) For example, electrochemistry of four polyferrocenylpolyphenylporphyrin compounds, including \(\text{H}_2\text{TFcP}\) (TFcP\(^{2–}\) = \(5,10,15,20\)-tetraferrocenylporphyrin(2–)), was investigated.\(^{40}\) The compounds showed stepwise Fe-based oxidations with the formation of mixed-valent species and the extent of electronic coupling was assessed as Class II in the Robin-Day classification on the basis of analysis of the IVCT band appeared in the NIR region. The mediation ability of the porphyrin core stems from the presence of porphyrin-cyclopentadienyl \(\pi\)-pathway in these compounds despite of the conformational flexibility of the Fe groups on the porphyrin core and iron–iron separation greater than 12 Å. In addition to the porphyrin compounds, introduction of Fe groups onto the framework of phthalocyanine is also achieved.\(^{45}\)
3.3. Polyferrocenyl Compounds with Extended Structures: Stars and Rings.

A number of polyferrocenes (oligoferrocenes), or ferrocenyl polymers, have been investigated in view from many aspects of chemistry, including electron transfer, recognition, sensing, and catalysis as well as application to molecular electronic devices. They have various structural types such as linearly-linked ferrocenyl wires, star-shaped dendritic polyferrocenes, and ring-shaped (cyclic) polyferrocenes. Theoretical treatment of the stepwise oxidation processes of these polyferrocene oligomers, depending on the structural type, has been developed by Aoki and the co-workers, and the theory has been successfully applied to the experimental systems.

A rigid ferrocenyl dendrimer, hexakis(ferrocenylethynyl)benzene, and its derivatives were synthesized (Fig. 7). These polyferrocenyl compounds were reversibly oxidized to their corresponding hexakis(ferrocenium) salts chemically or electrochemically. For example, a six-electron oxidized, hexacationic dendrimer has been prepared by reacting with a six-fold excess of ferrocenium hexafluorophosphate in CH$_2$Cl$_2$. The electronic properties for these compounds are associated with intramolecular communication and also electrostatic interactions between the ferrocenyl groups. On their CVs, the Fe-based redox patterns proved to be highly dependent on the nature of electrolyte counterions and the number of methyl substituents on the Fe groups. CVs of the dendrimer in CH$_2$Cl$_2$ showed a single wave when n-Bu$_4$NP$_6$ was used as the supporting electrolyte, but the wave splits into three when n-Bu$_4$NBArF was used as the supporting electrolyte (BArF = B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4$) (Scheme 3) whose interesting ion-pairing properties and application in electrochemistry have been recently described. The fact that the splitting was only observed with n-Bu$_4$NBArF indicates that the splitting does not result from electronic communication among the redox centers but from electrostatic effects that arise from ion pairing with the electrolyte anion upon oxidation of the neutral compound. The hexakis(ferrocenyl)benzene which has a single methyl group on each cyclopentadienyl ring exhibits six one-electron-oxidation steps in CH$_2$Cl$_2$ containing n-Bu$_4$NBArF as a supporting electrolyte. This indicates that the rigidly planar molecule bearing redox-active Fe groups undergo redox reactions that are very sensitive to ion-pairing electrostatic effects.
Electrostatic effects are also important to describe oxidation pattern seen in ring-shaped oligoferrocene systems. A series of cyclic polyferrocenylsilanes from dimer to heptamer, \([\text{Fe}(\eta^2-\text{C}_5\text{H}_4)_{2}\text{Si}(\text{CH}_3)_{2}]_n\) (\(n = 2–7\); Fig. 8),\(^{35}\) which were separated by column chromatography, showed stepwise oxidation due to mutual “electrostatic” interactions between the redox-active units. Remarkably, it was found that two reversible redox processes of varying intensities were observed for cyclic oligomers containing an even number of Fc centers, while three reversible redox processes of varying intensities were observed for cyclic oligomers containing an odd number of Fc centers (Fig. 9). This was well described by considering the effect of adjacent positive charge produced during the oxidation processes. A stronger through-space interaction, \(e.g.,\) an increased spread of \(E_{1/2}\) potentials, is observed as the greater constrain of the cyclic structure (the smaller separation of the iron centers) is achieved. Also, the electronic communication may be influenced by the nature of the spacer group with varying size (controlling metal-metal separation) and polarizability (influencing the dielectric constant).

3.4. Medium Effects.

Redox potentials can be influenced by the nature of solvents and electrolyte anions, and this aspect is apparently important in discussing the stability of the mixed-valent states \(\text{(e.g., the extent of metal-metal interaction) of binuclear and multinuclear complexes of interest.} \) There is a systematic investigation on the solvent and electrolyte effects on the multistep redox behavior of a tetraferrocenyl complex \(\text{Ni(S}_2\text{C}_2\text{Fc}_2)_2\) where \(\text{Fc} = \text{Fe(C}_5\text{H}_5)(\text{C}_5\text{H}_4)\) (Fig. 10).\(^{64,65}\) The differential-pulse voltammograms (DPVs) showed how the four Fc-based oxidations of this compound become spread out in \(\text{CH}_2\text{Cl}_2\) as the supporting electrolyte is changed (Fig. 11); the spread, expressed as \(E_{1/2}(4) - E_{1/2}(1)\), increased from 292 mV for \(n\)-Bu\(_4\)NPF\(_6\) to 510 mV for \(n\)-Bu\(_4\)NB(C\(_6\)F\(_5\))\(_4\) to 682 mV for NaBArF, an increase of almost 400 mV upon changing from a traditional anion (PF\(_6^–\)) to so-called weakly-coordinating anions (B(C\(_6\)F\(_5\))\(_4^–\), BArF\(_–\)). The cathodic waves, containing two one-electron processes, are also significantly tuned by the nature of cations in the supporting electrolytes \((n\)-Bu\(_4\)N\(^+\), Na\(^+\)) and solvents (CH\(_2\)Cl\(_2\), THF, anisole). By systematically changing solvents and supporting electrolytes,
the authors have proposed a formulation of a model for medium effects on $\Delta E_{1/2}$ values. In order to achieve the largest values of $\Delta E_{1/2}$, the use of a lower polarity solvent of low donor number (or low acceptor number), a weakly ion-pairing electrolyte anion (or cation), a strongly ion-pairing electrolyte counterion (or counteranion), and a decreased concentration of supporting electrolyte, is favored.

4. Redox Chemistry of Metallodendritic Systems.

Metallodendrimers are a new class of metal-containing macromolecules. The introduction of metal ions onto the periphery or within dendrimers allows access to novel materials with interesting electronic, magnetic, and optical properties. A great majority of metallodendrimers are peripherally metallated organic dendrimers, but dendrimers containing transition-metal sites in every generation are still rare. Ruthenium-acetylide dendrimers with the number of Ru$^{II}$ sites ranging from three, nine (first generation), and twenty-one (second generation) which are bridged by tris(4-ethylphenyl)amine were prepared (Fig. 12). CVs of the first, and second generation dendrimers recorded in 0.1 M n-Bu$_4$NPF$_6$–1,2-dichloromethane reveal well-resolved three waves, in which two waves at lower potential are assigned to Ru-based processes (Ru$^{II}$/III) and the remaining wave at the highest potential is assigned to ligand-based processes (triphenyl-amine moiety). Splitting behavior of the Ru-based processes indicates that the tris(4-ethylphenyl)amine is a good mediator for intramolecular electron transfer among the Ru sites.

Owing to the substitution-inert nature of both Ru$^{II}$ and Ru$^{III}$, stepwise construction of redox-active dendrimers from robust Ru-containing building blocks is further achieved. For example, a dendrimer containing 30 ruthenium centers in a single molecule (or containing ten [Ru$_3$O(CH$_3$COO)$_6$]$_3$ cores; Fig. 13) and the related system have been prepared via the convergent synthetic approach.

More recently, the synthesis and characterization of redox-active heterometallic dendrimers have been reported. These electrochemically-robust metallodendritic systems can be used as molecular batteries. A series of dendrimers with amidoferrocenyl units attached to diaminobutane-based poly(propyleneimine) through alkyl chains showed electrochemical responses to anions in organic media (0.1 M n-Bu$_4$NPF$_6$–dichloromethane). Immobilization of these ferrocenyl dendrimers onto Pt or glassy carbon electrodes allows their anion sensing (HSO$_4^-$, PO$_4^{3-}$) to be performed successfully in both organic (0.1 M n-Bu$_4$NPF$_6$–dichloromethane) and aqueous (0.1 M LiClO$_4$–H$_2$O) media. Heterometallic dendrimers comprising of ferrocenyl and Co(CO)$_3$ groups attached to the periphery show reversible single-step multi-electron redox waves due to the individual redox sites (e.g., iron or cobalt). Communication between these redox sites are very weak.

5. Metal-Metal Interactions in Ligand-Bridged Molecular Triangles and Squares.

The coordination-driven self-assembly is a hot subject in supramolecular chemistry. For example, the use of a four or six-coordinate metal fragment that provides 90°-coordination sites and a linear linker in a 1:1 ratio yields

![Fig. 12 Chemical structures of ruthenium-containing dendrimers.](image-url)
the [4 + 4] molecular square.\(^{70}\) With various topologies of metal fragments and organic linkers, this method has afforded much examples of 2D and 3D discrete compounds.\(^{74-78}\) A ferrocenyl-containing 120°-di-Pt\(^{II}\) acceptor and a 120°-dendritic donor were combined to form a giant cyclic structure containing multiple ferrocenyl moieties.\(^{79}\) Electrochemical studies indicated that all of the ferrocenyl groups immobilized to the dendritic molecules are redox-active but they behave independently.

This directional bonding approach, however, does not always give a desired compound selectively due, at least in part, to flexibility of organic ligands and metal-ligand coordination bonds. There are some cases in which the combination of a 90°-metal precursor and a linear linker gives rise to the formation of not only a geometrically expected molecular square but also an unexpected molecular triangle (Fig. 14), that is dependent on synthetic conditions employed. For example, when a 90° precursor trans-[RuCl\(_2\)(DMSO)\(_4\)] was reacted with an equivalent amount of pz, which is normally regarded as a rigid linear bridge, a molecular triangle was formed in a higher yield than the molecular square.\(^{82}\)

In view from metal-metal communication, electrochemistry of such metallacycles where the individual redox-active metal centers are located equivalently in a single molecule is of considerable interest. A mixed-valent molecular square [((cyclene)\(_4\)Ru\(_4\)(μ-pz))\(^{9+}\) (cyclene = 1,4,7,10-tetraazacyclododecane) in which the formal oxidation states of the four Ru centers is described as Ru\(^{II}\)_3Ru\(^{III}\)_1 was synthesized and structurally characterized.\(^{83}\) Cyclic voltammetry of the molecular square revealed a single quasi-reversible reduction of the square to form a fully-reduced \{Ru\(^{II}\)_4\}^8+ species and successive three-step oxidations to form \{Ru\(^{II}\)_2Ru\(^{III}\)_2\}^{10+}, \{Ru\(^{II}\)_3Ru\(^{III}\)_3\}^{11+}, and fully-oxidized \{Ru\(^{III}\)_4\}^{12+}. The significant stability of the 9+ species is noteworthy, where the comproportionation constant for the redox reaction (Eq. 5) was \(K_{\text{com}} = 10^{8.9}\), which is fairly larger than that for the Creutz-Taube ion (\(K_{\text{com}} = 10^{6.6}\)).

\[
{\text{Ru}}^{II}_4^{8+} + \text{Ru}^{II}_2\text{Ru}^{III}_2^{10+} \rightleftharpoons 2\text{Ru}^{II}_3\text{Ru}^{III}_3^{11+} \quad \text{Eq. 5}
\]

When 4,4'-bipyridine (4,4'-bpy) was used as a bridging ligand, a molecular triangle was also isolated.\(^{84}\) X-ray crystallography revealed that in the molecular triangle the angle of N\(_\text{bpy}\)–Ru–N\(_\text{bpy}\) (83.7(3)°) is significantly deviated from 90° with the Ru ••• Ru separation of 11.264 Å, which is slightly shorter than that of the molecular square (11.34 Å). Cyclic voltammetry of the molecular triangle [(cyclene)Ru\(_4\)(4,4'-bpy)]\((\text{PF}_6)_4\) showed reversible redox processes where three one-electron transfer reactions occur.
at $E_{1/2} = 0.207, 0.324, \text{ and } 0.434 \text{ V (vs. Fe/Fe}^+)\) that are assigned to the $6+/7^+, 7+/8^+, \text{ and } 8+/9^+$ couples, respectively, indicating the presence of electronic communication between the Ru centers with $K_{\text{com}}$ values of $10^{2.0}$ and $10^{1.9}$ for $\{\text{Ru}^{II}_{2}\text{Ru}^{III}_{2}\}^{7+}$ and $\{\text{Ru}^{II}\text{Ru}^{III}_{3}\}^{8+}$, respectively. These values are large among precedent 4,4'-bpy-bridged complexes. This is associated, in part, with the restricted rotation of 4,4'-bpy in the triangular system as deduced from the solid-state structure. It was found that the molecular square [(cyclene) Ru$_4$(4,4'-bpy)$_4$](CF$_3$SO$_3$)$_8$ exhibited a diminished degree of electronic coupling.

When a metal and bridging ligand are suitably chosen, the construction of molecular squares that show surprisingly large metal-metal coupling is possible. A mixed-valent tetranuclear iron complex $\{\text{Fe}^{II}_{2}\text{Fe}^{III}_{2}\}^{0}$ was prepared (Fig. 15a). This molecular square underwent successive one-electron redox reactions in CH$_3$CN (Fig. 15b). The redox potentials span in a wide potential region with enormously large $K_{\text{com}}$ values for the mixed-valent states ($4.07 \times 10^6, 3.63 \times 10^{13}, \text{ and } 1.95 \times 10^7$, for the +1, +2, and +3 species, respectively). Magnetic susceptibility measurements indicated the presence of two low-spin Fe$^{II}$ sites and two low-spin Fe$^{III}$ sites in the ground state, at room temperature but at low temperature there was a weak antiferromagnetic interaction between two Fe$^{III}$ sites. Considering the weak antiferromagnetic coupling and the inherent electrostatic repulsion of charge within the square framework, occupation of the Fe$^{II}$ sites at the opposite corner of the square with two-fold degenerate states was proposed. Two split IVCT transitions for the $\{+2\}$ mixed-valent state ($\nu_1 = 5600 \text{ cm}^{-1}$ and $\nu_2 = 7920 \text{ cm}^{-1}$) were well described by considering the multi-dimensional electron transfer theory, and may be regarded as an excellent molecular component for QCA devices (see Section 6), in which two binary states can be exchanged at room temperature.

A cyanide ion (CN$^-$) is also a good ligand to bridge two metal centers to form a well-defined mixed-valence molecular squares. The synthesis, structures, and electrochemistry of $[\text{Fe}_{4}(\mu-\text{CN})(\text{bpy})_8]^{4+}$ ($[\text{Fe}^{II}_{4}]^{4+}$) and its mixed-metal analogs $[\text{Fe}^{II}_{3}\text{Co}^{III}]{_2}^{4+}$ and $[\text{Fe}^{II}_{3}\text{Ru}^{III}]{_2}^{4+}$ were thoroughly investigated. The compounds may be viewed as molecular building blocks of Prussian Blue. The intermetallic electronic coupling in these homometallic and heterometallic molecular squares was assigned as a Robin-Day Class II on the basis of their controlled-potential optical absorption spectroscopy. Their electrochemistry along with other interesting physicochemical properties including spin crossover phenomena have been recently reviewed.

### 6. Applications and Prospects

The use of mixed-valence compounds for QCA was proposed by Lent and the co-workers. The original idea of QCA stems from constructing islands of metal atoms locating at each corner of a square on a surface. When two extra electrons are added to the square, they may occupy two opposite corners owing to electrostatic repulsive force (Fig. 16a). These two forms correspond to two energetically degenerate but distinguishable quantum states and serve as a binary code. The device function of QCA is achieved when each QCA cell is assembled into the one-dimensional array on a surface (Fig. 16b). An input (or bias; shown as an empty arrow in Fig. 16b) on one end will result in switching the initial electron configuration of the cell and the signal may be transmitted to the neighboring cell due to electrostatic reason. Like dominoes, the signal travels to achieve again the lowest-energy state. On the basis of the idea, the QCA is supposed to work without actual current flow. In addition to metal nanoparticles, mixed-valent tetranuclear and dinuclear complexes (which are components of the square) are candidates for “molecular” QCA (MQCA).
Theoretical aspects have been further developed recently.\textsuperscript{96,97} The next experimental challenge for MQCA definitely may involve to develop techniques to locate the cells in the form of a wire in a desired location and hopefully in a defined length on a solid surface.

One of new directions of mixed-valent complexes elaborated from our laboratory is shown here. Compounds that absorb light in the near infrared (NIR) region have attracted much attention due to their potential applications to optoelectronic devices, Q-switching lasers, and telecommunication. Since the NIR light (800–2500 nm) from sunlight is a principal origin of warming, mixed-valent complexes showing a strong IVCT band normally found in the NIR region may be good chromophores for heat shielding, to which less attention has been paid so far from coordination chemists. A polymer (polyvinyl alcohol; PVA) film that contains mixed-valent oxo-centered triruthenium clusters with strong NIR absorption in the Ru\(_3\)(II,III,III) states have been prepared.\textsuperscript{98} This polymer actually exhibits heat shielding effect, rendering the increase of temperature to a more diminished extent relative to a reference polymer that contains a NIR-transparent Ru\(_3\)(III,III,III) cluster (Fig. 17). The heat shielding property can be tuned by controlling the absorption energy and intensity of the chromophore by modifying three ancillary ligands or six bridging carboxylates on the cluster framework.\textsuperscript{99–101} The work demonstrates an unprecedented utility of mixed-valent transition-metal complexes and is quite appealing not only to coordination chemistry but also to industry. The redox-state-dependent shielding effect could be applied to switching materials if electrochemical operation is applied to the polymer film.

As the accumulated results in this review article demonstrate, the chemistry of mixed-valent complexes, starting from the classical Creutz-Taube ion to new evolving examples of ligand-bridged clusters with various nuclearity, geometric shape, and electronic structures is still continuing to grow and provides insight into electronic and physical properties of multimetallic coordination compounds. While the ferrocenyl groups have played a central role in the mixed-valence coordination chemistry so far, new compounds with various redox groups have been explored recently. In these systems, geometric and electronic structures of bridging ligands (or bridging metals) that link two redox-active metal centers play a decisive role in determining the extent of valence delocalization. In this context, a new aspect can be seen in a recent report which describes metal-metal coupling via hydrogen bonds.\textsuperscript{102} Finally, in relation to the fabrication of putative nanoelectronic devices from molecular species, chemistry on surface attachment and organization of mixed-valence compounds at a solid/surface is an important issue to be developed by coordination chemists. With the aid of recent advancement in scanning tunneling microscopy (STM) techniques in solution or under electrochemical conditions,\textsuperscript{103–108} a direct visualization of mixed-valent clusters as well as kinetic probing of ligand-substitution reactions have become possible at a solid/liquid interface, and such a new interdisciplinary research has just begun.\textsuperscript{109}
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