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Abstract

Substitutionally inert ruthenium complexes bearing benzimidazole derivatives have unique electrochemical and photochemical properties. In particular, proton coupled electron transfer (PCET) in ruthenium–benzimidazole complexes leads to rich redox chemistry, which allows e.g. the tuning of redox potentials or switching by deprotonation. Using the background knowledge from acquired from their solution-state chemistry, Ru complexes immobilized on electrode surfaces have been developed and these offer new research directions toward functional molecular devices. The integration of surface-immobilized redox-active Ru complexes with multilayer assemblies via the layer-by-layer (LbL) metal coordination method on ITO electrodes provides new types of functionality. To control the molecular orientation of the complexes on the ITO surface, free-standing tetrapodal phosphonic acid anchor groups were incorporated into tridentate 2,6-bis(benzimidazole-2-yl) pyridine or benzene ligands. The use of the LbL layer growth method also enables “coordination programming” to fabricate multilayered films, as a variety of Ru complexes with different redox potentials and pKₐ values are available for incorporation into homo- and heterolayer films. Based on this strategy, many functional devices, such as scalable redox capacitors for energy storage, photo-responsive memory devices, proton rocking-chair-type redox capacitors, and protonic memristor devices have been successfully fabricated. Further applications of anchored Ru complexes in photoredox catalysis and dye-sensitized solar cells may be possible. Therefore, surface-confined Ru complexes exhibit great potential to contribute to the development of advanced functional molecular devices.

Keywords: Ru benzimidazole complex, surface immobilization, layer-by-layer assembly, molecular devices, redox chemistry, proton-coupled electron transfer (PCET), heterolayer, multilayer film, memory, phosphonic acid, redox capacitor, protonic memristor

1. Introduction

Ruthenium is a precious metal that belongs to the platinum-group elements [1]. As ruthenium can adopt various oxidation numbers, its coordination complexes adopt a wide variety of oxidation states from -II to VIII [2]. When nitrogen-based donor ligands are coordinated to a central ruthenium atom, the resulting ruthenium
complexes generally prefer the +II and + III oxidation states, but occasionally also adopt the +IV and + V states. Arguably the most studied Ru complexes with nitrogen-based donor ligands are those that contain the hexaammineruthenium dication, [Ru(NH$_3$)$_6$]$^{2+}$, and the tris(2,2'-bipyridine)ruthenium(II) dication, [Ru(bpy)$_3$]$^{2+}$. [Ru(bpy)$_3$]$^{2+}$ was first reported by Burstall [7] and is easily obtained from the reaction of RuCl$_3$•nH$_2$O with an excess amount of bpy in aqueous ethanol. [Ru(bpy)$_3$]$^{2+}$ exhibits a stable low-spin $t_{2g}^6$ electronic configuration as well as a reversible one-electron oxidation at +1.29 V (vs SCE) and successive one-electron reductions at −1.33 V, −1.52 V, −1.76 V, and −2.4 V vs. SCE; the oxidation is a Ru(II/III) metal-center-based process, while the reductions occur on the bpy ligands. [Ru(bpy)$_3$]$^{2+}$ exhibits a metal-to-ligand charge transfer (MLCT) band at 452 nm and bright luminescence at 612 nm (lifetime: 600 ns) under MLCT excitation. This luminescence arises from the triplet MLCT photoexcited state, which allows this complex to serve as a photosensitizer for a wide scope of photoenergy conversion processes and as a photocatalyst for organic transformations [8]. Therefore, it is hardly surprising that during the past five decades, numerous studies on photoactive [Ru(bpy)$_3$]$^{2+}$ complexes have been reported [3].

For example, replacing one of the bpy ligands in [Ru(bpy)$_3$]$^{2+}$ with an N-heteroaromatic ligand comprising a benzimidazole and a pyridine group shifts the Ru(II/III) oxidation potential in negative direction because benzimidazole is a stronger σ-donor and weaker π-acceptor than pyridine [9]. Furthermore, the coordinated benzimidazole N–H imino group acts as a Brønsted acid, and the corresponding deprotonated benzimidazolate site can coordinate to another metal ion (Figure 1) [10]. Protonated or N-alkyl benzimidazolium ions can act as precursors for N-heterocyclic carbene (NHC) metal complexes [11, 12]. The representative pyridine-containing ligands 2,2'-bipyridine (bpy) and 2,2',2''-terpyridine (tpy) form chelate complexes with bidentate and tridentate coordination modes. When one or two pyridine groups are replaced with benzimidazole, the resulting bidentate- and tridentate-coordinating ligands are known as 2-(2-pyridyl)benzimidazole and 2,6-bis(benzimidazol-2-yl)pyridine, respectively (Figure 2) [13, 14].

![Figure 1](image1.png)

*Figure 1.* Coordination modes of pyridine and benzimidazole as ligands.
This chapter focuses on the molecular design of ruthenium complexes with N-heteroaromatic ligands, particularly benzimidazole derivatives. In Ru–benzimidazole complexes in aqueous solution, the solution pH strongly affects the Ru(II/III) oxidation potential, which is derived from the proton-coupled electron transfer (PCET) reaction in solution [15]. The proton-responsiveness of Ru–benzimidazole complexes has been exploited to obtain switching functionality in multinuclear Ru complexes [16, 17]. In addition, ligand modification via N-alkylation of the benzimidazole N–H imino group has been used to achieve the anchoring of redox-active Ru complexes [18, 19], and the layer-by-layer (LbL) assembly of Ru complexes on indium-tin oxide (ITO) surfaces toward molecular electronic devices [20–22].

**Figure 3** presents a schematic illustration of our conceptual approach for molecular devices based on surface-confined Ru complexes with electron/proton-responsiveness.
2. Molecular design of functional Ru complexes with benzimidazole ligands

2.1 Bridging ligands that contain benzimidazole groups

Benzimidazole ligands can be synthesized by the Phillips condensation reaction between an organic carboxylic acid or nitrile and o-phenylenediamine [23]. Figure 4 shows the structures of benzimidazole ligands bridging two Ru centers that have been used by our group [17, 24–26] and others [27, 28] for the preparation of dinuclear Ru complexes. Depending on the chemical structure of the linker moiety, significant electronic coupling between the two ruthenium ions is possible. In addition, the oxidation processes of the Ru centers in aqueous solution involve PCET reactions, resulting in switching of the metal–metal interaction via the change in electron density on the conjugated linker ligand.

2.2 Introducing anchor groups in benzimidazole ligands

Surface modification plays an important role in controlling the electron-transfer events and chemical reactivity in photocatalysis, as well as the charge-transport process in heterojunctions. Recently, several reviews of the applications of surface modification toward dye-sensitized solar cells and electrochemical catalysts for hydrogen/oxygen-evolution reactions have been published [21, 29–34], showing the importance of such interdisciplinary research. In the area of solar-energy conversion, Grätzel-type dye-sensitized solar cells composed of mesoporous TiO$_2$ on fluorine-doped SnO$_2$ (FTO) with immobilized Ru complexes that contain 2,2’-bipyridyl-4,4’-dicarboxylate and other bpy-derived ligands have been developed [35]. Interestingly,

![Diagram of benzimidazole ligands bridging two Ru centers in bis-bidentate or bis-tridentate coordination modes.](image)
the electron-injection efficiency from the photoexcited-state Ru complex to TiO\textsubscript{2} was found to strongly depend on the anchoring group [34, 36, 37].

Given that the adsorption strength of a Ru complex on a surface depends on the combination of the anchoring group and the surface material, judicious selection of both is necessary for effective surface functionalization. Recently, indium-tin oxide (ITO)-coated glass or polymer substrates have been employed in a wide variety of electronic display devices such as organic light-emitting diodes (OLEDs) [38]. Transparent ITO electrodes are also employed as cell windows for spectroelectrochemistry. Therefore, ITO is a suitable substrate for monitoring both the electrochemical and spectrochemical changes in redox-active Ru complexes immobilized on its surface. The phosphonic acid group, which is known to immobilize on ITO electrodes, has been employed to anchor the Ru complexes [39]. Furthermore, organic phosphonic acids are known to bind zirconium(IV) ions to form a solid two-dimensional layer structure, [40], which demonstrates their suitability for use in a layer-by-layer growth method based on redox-active metal complexes. Therefore, we developed several new tridentate benzimidazole ligands with phosphonic acid or phosphonate ester anchor groups (Figure 5). Alkylation of the imino N–H groups of the benzimidazole moieties using bromoalkyl-diethylphosphonate derivatives furnished chelating benzimidazolyl ligands with ethyl-protected phosphonates, which were used for the synthesis of Ru complexes [41]. After the ethyl-protected phosphonate Ru complexes had been purified, the diethyl phosphonate groups were deprotected to provide the corresponding Ru complexes with phosphonic acid groups. In particular, the tridentate ligand \textit{XP} (Figure 5) contains several methylene groups on its side-arms; these methylene moieties are sterically hindered, thus fixing the conformation of the phosphonic acid anchor groups upon surface immobilization.

2.3 Molecular design of redox-active Ru complexes with anchor groups

Ru complexes are substitutionally inert, and the octahedral coordination geometry around the Ru ion is maintained throughout the Ru(II/III) redox reaction. Therefore, they can be immobilized on a surface to design redox-active molecular devices. When three bidentate ligands are coordinated to an octahedral Ru complex, the formation of \(\Delta\) and \(\Lambda\) optical isomers is possible, but in the case of Ru complexes surrounded by two tridentate ligands with \(C_{2v}\) symmetry, no optical isomers do not exist. Hence, surface-confined Ru complexes that contain tridentate ligands with \(C_{2v}\) symmetry such as 2,6-bis(benzimidazolyl)pyridine with phosphonic acid anchors are often selected for surface immobilization [21, 42]. Furthermore, the molecular orientation of Ru complexes self-assembled on a surface is crucial to the construction of further

![Figure 5](image-url). Chemical structures of benzimidazole-containing ligands with phosphonic acid anchor groups and their abbreviations.
layered structures. To maintain the vertical orientation of the Ru complexes on a surface, free-standing multipodal anchor groups with phosphonic acid have been developed over the last two decades. Several examples are shown in Figure 6 [21, 43–46].

together with our multipodal tridentate benzimidazole ligand with phosphonate anchors, XP. Figure 7 shows a new series of rod-shaped Ru complexes with 2,6-bis (benzimidazolyl)pyridine moieties and bi- or tetrapodal phosphonic acid groups at both ends that have been reported by our group. Mononuclear Ru complex 10 exhibits a spherical-shaped structure around the central Ru ion, while the other dinuclear Ru complexes 8, 9, 11, and 12 exhibit a rod-like structure with a Ru–Ru axis [21, 43]. When the dinuclear Ru complexes are immobilized on a surface, the Ru–Ru axis can be oriented vertically or horizontally relative to the surface plane. In AFM measurements, the obtained molecular heights of the dinuclear Ru complexes 9, 10, and 11 immobilized on an ITO surface were consistent with the predicted heights for the vertical orientation of the dinuclear Ru complexes at the ITO surface. Ru complexes 8–12 can be dissolved in aqueous solution by adjusting the solution pH, given that the phosphonic acid groups at both ends of these act as polybasic acids.

3. Characterization and functionality of surface-immobilized redox-active Ru complexes

3.1 Surface modification by Ru complexes bearing phosphonic acid anchors

When Ru complexes bearing phosphonic acid anchors are immobilized on an ITO or mica surface by immersion of the substrate into a solution of the Ru
complex, the surface coverage of the Ru complex is dependent on the immersion time and the concentration of the complex in the solution. The temporal evolution of the surface coverage can be analyzed using the kinetic Langmuir equation (Eq. (1)), and curve fitting with a rate constant parameter, $k$.

$$ \Gamma_t = \Gamma_s \left(1 - \exp\left(-kC^*t\right)\right) \quad (1) $$

Here, $\Gamma(t)$, $k$, $C$, and $t$ refer to the surface coverage, rate constant, concentration of the Ru complex, and time, respectively [33, 46]. A typical kinetic plot for a Ru–XP complex with an acridine group at the top is shown in Figure 8. This surface-immobilized Ru–XP complex is able to capture double-stranded DNA from solution [46].

Another chemical approach to evaluate the surface coverage is using the thermodynamic Langmuir isotherm based upon the concentration dependence of the adsorption of the Ru complex.

$$ \frac{\Gamma_i}{\Gamma_s} = \exp\left(\frac{\Delta \text{G}_{\text{ads}}}{RT}\right)C_B \quad (2) $$

Here, $\Gamma_i$, $\Gamma_s$, $C_B$, and $\Delta \text{G}_{\text{ads}}$ refer to the surface adsorption at a given concentration, the adsorption at saturation, the concentration of the bulk solution, and the free energy of adsorption, respectively. The adsorption of a Ru complex on a mica and ITO surface can be fitted with the typical Langmuir isotherm model. The free energy of adsorption for Ru complex 9 was found to be $-33.4$ kJ/mol.

In recent years, several binding modes for the adsorption of phosphonic acid groups on metal oxides have been proposed based on intensive studies using polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations in recent years, and the bidentate or tridentate binding modes are considered to be most probable (Figure 9) [30, 32, 34, 44, 47]. The optimum solution pH value for the adsorption of Ru complexes 8–12 depends on the complex; i.e., pH = 6 is optimal for complexes 8–11, while pH = 4 is better for complex 12.

Atomic force microscopy (AFM) measurements have been used to provide clear surface images depicting the adsorption of these Ru complexes, particularly the surface morphology (e.g., height and surface coverage). Figure 10 shows AFM images of Ru complex 9 on a flattened ITO surface. The samples were prepared using two different immersion conditions, i.e., a dilute solution of the Ru complex with a short immersion time (1 μM; 10 min) and a higher concentration solution with a longer immersion time (25 μM; 3 h). As shown on the left in Figure 10, for the dilute...
condition, scattered dots were observed on the surface. The average height of the dots was approximately 4 μm, which is consistent with the height that was predicted for vertically oriented complex 9 using a molecular model. The AFM image on the right in Figure 10 shows that the surface was fully covered with spherical domains with a diameter of 20–50 μm when the concentrated conditions were used.

One advantage of ITO electrodes is that they enable the use of UV–vis spectroscopy to monitor the surface immobilization process. Ru(II) complexes bearing N-heteroaromatic ligands exhibit a relatively strong metal-to-ligand charge transfer (MLCT) band in the visible wavelength region. In particular, the temporal changes during the immobilization or multilayering processes of such complexes on modified ITO substrates are easily monitored via the absorbance changes in the UV–vis spectra. Furthermore, electrochemical methods such as cyclic voltammetry (CV) can be used to determine the surface coverage of redox-active Ru complexes immobilized on an ITO electrode [48].

3.2 PCET reaction of Ru-benzimidazole complexes in solution and on ITO electrodes

Ru complexes with benzimidazole derivative ligands act as Brønsted acids and exhibit proton-coupled electron transfer (PCET) reactions in aqueous solution [49, 50].
For example, \([\text{Ru(mbibzim)(bibzimH}_2]^2^+ (13) \) (mbibzim = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine and bibzimH\(_2\) = 2,6-bis(benzimidazole-2-yl)pyridine) behaves as a dibasic acid, as shown in Figure 11. The Ru(II/III) oxidation potential of 13, which results from a PCET reaction, strongly depends on the pH-value (2 < pH < 9) in a Britton–Robinson buffer/CH\(_3\)CN(1:1 v/v) solution \([14, 49, 50]\). The PCET reaction of 13 can be described by the square scheme in Figure 12, in which complex 13 is abbreviated as Ru–LH\(_2\). This reaction involves both electron transfer and proton-transfer equilibria. In the half-wave potential/pH plot of 13, the so-called Pourbaix diagram, the half-wave potential is gradually shifted in the negative potential direction with increasing solution pH (Figure 13). Based on this diagram, the pK\(_a\) values of 13 were determined to be 6.31 and 7.94 for the Ru(II) oxidation state, and <2 and 3.60 for the Ru(III) oxidation state. When the central pyridine group in the bibzimH\(_2\) ligand is replaced with a cyclometallated phenylene group, the resulting Ru complex 14 shows a lower Ru(II/III) oxidation potential than complex 13; the pK\(_a\) values of 14 also increase compared to those of 13, i.e., to 10.91 and >12 for the Ru(II) oxidation state and to 6.46 and 9.15 for the Ru(III) oxidation state \([51]\).

In biological systems, protons play a very important role in reactions and energy storage. Proton gradients are the driving force for the synthesis of ATP in biological membranes. Applications of proton gradients in energy storage in materials chemistry have shown that PCET chemical systems can be used for energy storage in redox batteries and capacitors. Ru complexes 13 and 14, which show PCET with different potentials and pK\(_a\) values in unbuffered aqueous solutions, have been used to construct two half-cells separated by a Nafion membrane \([51]\). The Pourbaix diagrams of complexes 13 and 14 are shown in Figure 14; the initial oxidation states of 13 and 14 were Ru(II) and Ru(III), respectively. Upon charging, the oxidation of 13 from the Ru(II) to the Ru(III) state releases the proton(s), while the reduction of 14 from Ru(III) to Ru(II) at the other half-cell captures the proton(s). As a result,

![Figure 11](image1.png)

Stepwise proton-transfer equilibria of Ru(II)(LMe)(LH\(_2\)) complexes (13: X = N; 14: X = C) that act as Bronsted dibasic acids. The total charge of the Ru complex is omitted.

![Figure 12](image2.png)

Square scheme of the electron–proton equilibria of Ru complexes 13 or 14 as dibasic acids. Numbers in parentheses indicate the Ru species present in the Pourbaix diagram in Figure 13.
The electrical energy was stored as a pH gradient between the half-cells. The concept of using a PCET system in this way had been implemented with organic quinone derivatives, [52] but its scope was extended to redox-flow batteries by using a pH-tunable Fe(III) azamacrocyclic complex as both the catholyte and anolyte based on the multiple protonated forms of the Fe complex [53].

The PCET chemistry of Ru complexes that contain benzimidazole derivatives in solution can be extended to surface-bound systems by attaching surface-anchoring groups to the Ru complexes as described in the previous section. Dinuclear Ru complexes 15, 16, and 17 (Figure 15) have N–H sites that can be deprotonated on the bridging ligand and the phosphonic acid anchoring groups at both ends. When 15 and 16 are assembled on an ITO electrode, the surface-immobilized redox-active Ru(II) complexes exhibit a well-defined CV response with a typical shape derived from adsorbed chemical species [20]. Figure 16 shows the CV responses that originate from the Ru(II/III) oxidation process of immobilized complex 15 at different pH values; these responses arise from a well-defined two-electron oxidation wave corresponding to the Ru(II)–Ru(II)/Ru(III)–Ru(III) PCET process in 15 [24]. Upon changing the pH of the aqueous solution was changed, Ru complexes 8–17 immobilize stably via the phosphonic acid groups on the ITO electrode at pH = 1.0–9.0, but at pH >9.5, the Ru complexes easily detached from the ITO surface.

Figure 13.
Pourbaix diagram of Ru complex 13 in CH₃CN/BR buffer (1/1 v/v) [51].

Figure 14.
Pourbaix diagram for a solution redox battery based on a pair of Ru complexes, 13 and 14, which both exhibit PCET reactions in CH₃CN/BR buffer (1/1 v/v).
The anodic peak current, $i_{pa}$, is expressed as shown in Eq. (3), where $n$, $\nu$, $A$, and $\Gamma$ represent the number of electrons, scan rate, electrode area, and surface coverage, respectively. Therefore, the anodic peak current for complex 15 is linearly proportional to the scan rate $\nu$, indicating that the Ru complex is a surface-bound species. The total area of the anodic wave is related to the surface coverage of the Ru complex, which was determined to be $0.80 \times 10^{-10}$ mol cm$^{-2}$.

$$i_{pa} = \frac{n^2F^2\nu}{4RT} A\Gamma$$

(3)

Given that the spectral change due to the redox reactions of a monolayer film of 15 on the ITO electrode can be observed by UV–vis spectroscopy, even surface-assembled monolayer films of Ru complexes on an ITO electrode can be detected.
Upon the oxidation of 15 under an applied potential of +0.8 V vs. Ag–AgCl at pH = 6.5, the differential absorption spectrum demonstrates strong bleaching of the MLCT band at 550 nm and π-π* transitions of the ligands at 364 nm, along with absorbance increases at 400 and ~750 nm, which are characteristic spectral features of Ru(III)–L complexes [24].

3.3 Fabrication of multilayer films based on Ru complexes by layer-by-layer (LbL) growth

Surface modification using a molecular monolayer film alone enables only a single set of functionalities to be incorporated, and the measurable physical quantities, such as optical absorption or current value, are very low due to the low molecular density on the surface. On the other hand, multi-layer modification has the advantages of allowing various molecular units to be deposited at the surface, achieving greater increases in physical quantities such as optical density and charge stored, and enables the integration of various functionalities at the interface [31]. Thus, the integration of functional metal complexes on an electrode holds great promise for applications in e.g., molecular-based devices for photochemical energy production/transduction, photocatalysis, and information storage, among other applications [54]. To achieve this integration, the LbL assembly method, in which multilayer structures are constructed via molecular interactions between two layers on a solid surface, is an appropriate technique [39]. LbL assembly using electrostatic interactions, [55], hydrogen bonding, and coordination metal–ligand bonds has been reported [21, 56]. Among these, structures based on metal-coordination assembly are robust toward environmental changes, such as variations in pH or ionic strength, in aqueous solution.

The formation of well-ordered zirconium(IV) bisphosphonate multilayer films is a well-known method for LbL assemblies on a solid surface that has been developed by Mallouk and others [40]. This method is based on the reconstitution of a two-dimensional layered compound, Zr(HPO₃)₂, on a gold surface via self-assembly of molecular units with metal ions. Starting from self-assembled 4-mercaptopbutylphosphonic acid on the gold surface as a primer layer, alternate immersion of the modified gold substrate into a zirconium(IV) oxychloride solution and a bisphosphonic acid solution leads to multilayer films composed of a two-dimensional zirconium–phosphonate framework structure via LbL growth [40].

Similarly, the rod-shaped Ru complexes 8–16 with polyphosphonic acid groups at both ends were immobilized by self-assembly on an ITO electrode. The polyphosphonic acids at one side of the complexes were attached to the ITO surface, while the other side of the polyphosphonic acid groups remained free to interact with metal ions in solution. Multilayer films of the Ru complexes could thus be obtained by successive alternate immersion in a zirconium(IV) ion and a Ru complex solution (Figure 17) [57]. The immobilized Ru film on the ITO substrate was monitored via UV–vis spectroscopy, CV, and the AFM-surface-scratching method throughout each stage of the LbL growth. The use of these monitoring techniques during LbL growth is shown in Figure 18 with the combination of Ru complex 11 and zirconium as an example.

In each physical measurement, the physical quantities, such as absorbance, amount of charge, and the height of the scratch increased linearly with increasing number of layers. Two types of growth models have been proposed for LbL growth from the surface-primer points via metal coordination on a solid surface (Figure 19) [59]. The first model involves dendritic divergent growth, which would result in an exponential increase in the physical quantities, while the second model involves linear growth of a layered structure. In the case of Ru complex 11,
the linear increase in the physical quantities such as absorbance indicates the formation of well-ordered two-dimensional multilayer films on the solid surfaces.

The use of the LbL method on a solid surface makes it possible to accumulate various molecular units with different chemical functionalities by adjusting the number of layers and metals in the multilayer films. Furthermore, the sequential order of the various complex units can be varied; the units can be arranged in order of descending or ascending potential or $pK_a$ to produce hetero-multilayer films. Such gradients in the layers play an important role in energy transduction. Therefore, “coordination programming” at the surface is possible via judicious choice of molecular units [60]. For example, when two different complexes A and B are assembled into a four-layered film on a solid substrate and a primer layer A is fixed as the first immobilized layer, seven combinations can be obtained by varying the order of the successive layers (substrate|ABAB, |AAAB, etc.). As a result, various films with different potential gradients can be created, and their rectification of electron transfer can be evaluated. Finally, in the fabrication of heterolayers using
metal-coordination via the LbL method by immersion in solutions of each component, it is important to ensure that each layer is segregated and that the components are not mixed with others within the layer. In particular, care should be taken using metal ions with substitutionally labile properties, such as Ni(II) and Co(II) ions.

3.4 Functionality of LbL-multilayer films based on Ru complexes

3.4.1 Electron-transfer rate in homo-multilayer Ru complex films on ITO electrodes

Measuring electron-transfer events in multilayer LbL films composed of redox-active Ru complexes on an ITO electrode is fundamental to determine whether electrons can be transmitted through the multiple layers of Ru complexes as the number of layers is increased.

CV measurements of homo-multilayer films of 11 (X = N) to evaluate their electron-transfer rate showed two one-electron oxidation waves. With increasing number of layers, the peak current during CV increased almost linearly. The peak-potential separation between the anodic and cathodic waves was unchanged at a scan rate of 0.1 V s⁻¹, but at 1 V s⁻¹, the separation increased with an increasing number of layers. Using Laviron’s procedure, [61] the heterogeneous electron-transfer rate between the Ru complexes in the layers and the ITO electrode was determined for different numbers of layers. The electron-transfer rates gradually decreased with increasing number of layers, and a small attenuation coefficient was obtained from the slope of the plots of ln(k<sub>app</sub>) as a function of the thickness of films (L). The dependence of the electron-transfer rate, k<sub>app</sub>, on the distance is expressed by the following equation:

\[ k_{app} = k^0 \exp \left\{ -\beta L \right\} \]

In addition, potential-step chronoamperometry (PSCA) measurements furnished a relatively small value for the apparent electron-transfer rate, k<sub>app</sub> (β = 0.014 Å⁻¹) [62].

Multi-layer films of ruthenium complex 9 were grown on an ITO substrate using hydrogen-bonding interactions. In these films, free-standing ruthenium complexes of 9 adsorbed on an ITO electrode via its tetrapod phosphonic acid anchors interacts with complexes of 9 that are dissolved in the solution via multiple hydrogen bonds between the free phosphonic acid groups at its surface and those of the complex 9 in solution at pH = 6. Surprisingly, the film thickness of the resulting multiply hydrogen-bonded system was controlled by the immersion time and the solution
The current–voltage ($I$–$V$) characteristics of the multilayered Ru film grown on ITO were measured with a sandwich-type two-terminal devices using the conductive polymer PEDOT:PSS as the top electrode. Based on the observed current, the value of the coefficient for the attenuation with increasing film thickness was relatively small ($\beta = 0.012$–$0.021 \AA^{-1}$) [43]. This small $\beta$ value for the multilayer Ru complex film system indicates that long-range electron transport can be expected to be possible even though the system exhibits low conductivity. To clarify the reason for the long-range electron transport in the Ru multilayer film despite its low conductivity, first-principles calculations using Green’s non-equilibrium function technique and theoretical analysis of the experimental results were performed. The results indicated that the metal centers covered with the $\pi$ electrons of the ligands become “stepping stone” sites that provide a resonant tunneling mechanism [43]. Small $\beta$ values were also reported for terpyridine-metal-complex nanowires produced by the sequential metal-coordination method [63].

3.4.2 Redox-active LbL multilayer films in redox capacitors

As portable electronic devices continue to proliferate, cost-effective cheap energy storage devices that are small, flexible, and low cost and provide high performance during the charging and discharging cycle are in high demand. Molecular-based supercapacitors are promising candidates in terms of these requirements. Redox-active Ru complexes are suitable for the fabrication of energy storage devices, since multilayer molecular Ru assemblies obtained via the LbL method can be scaled by increasing the number of layers, which leads to enhancement of the electrical capacitance in such films [57].

The charge–discharge properties of a sixty-five-layer film of Ru complex 11, ITO|(Ru complex 11)$_{65}$, were examined under galvanostatic experimental conditions by applying various constant current densities from 10 to 100 $\mu$A cm$^{-2}$. The galvanostatic charge and discharge curves show two small plateaus at 0.12 V and 0.37 V vs. Pt, which correspond to two reversible Ru(II)/Ru(III) redox processes (Figure 20). A maximum capacitance of 92.2 F g$^{-1}$ was found at an applied current density of 10 $\mu$A cm$^{-2}$, but the capacitance decreased to 63.3 F g$^{-1}$ at the highest

![Figure 20](image.png)
current density of 100 μA·cm⁻² (Figure 20). Stability tests of the Ru multilayer films (>1000 galvanostatic charge–discharge cycles) showed a capacitance retention of 72% [57].

3.4.3 PCET reactions in Ru-multilayer films for energy storage devices

PCET reactions can be used in energy-storage devices such as redox-flow batteries or two half-cells in unbuffered aqueous solution as described in Section 4.2. The frameworks of dinuclear Ru complexes 16 and 17 are basically formed by chemical modification of the mononuclear Ru complexes 13 and 14 via the C–C coupling of two 13 or 14 units. Thus, the PCET behaviors of complexes 16 and 17 were almost the same as those of 13 and 14, except that the number of electrons involved in the PCET reaction was doubled to result in a two-electron process due to the C–C coupling of two molecular units of 13 and 14 and the surface immobilization on an electrode. The Ru complexes 16 and 17 were immobilized by the LbL method on an ITO electrode and applied in a redox capacitor device, in which an aqueous solution was sandwiched between two electrodes composed of multilayer films of 16 and 17 to evaluate the cell performance (Figure 21) [20]. Under galvanostatic conditions at a constant current density of 10 μA·cm⁻², stable charge–discharge behavior occurred, as shown in Figure 21.

During the charging process, the multilayer 16 acted as the anode and the following oxidation reaction proceeded, resulting in the release of protons:

\[
\text{Ru(II)}_2\text{L}_2\text{H}_2 \rightarrow \text{Ru(III)}_2\text{L}_2 + 2e^- + 2\text{H}^+. \tag{5}
\]

At the same time, the multilayer electrode of 17 acted as a cathode, and the following reduction took place, resulting in the capture of protons:

\[
\text{Ru(III)}_2\text{L}_2\text{H}_3 + 2e^- + \text{H}^+ \rightarrow \text{Ru(II)}_2\text{L}_2\text{H}_4. \tag{6}
\]
where 16 and 17 are represented as Ru₂L₃H₄ and Ru₂L₃H₅, and L₃H₄ and L₃H₅ indicate the bridging ligand bearing the indicated number of protons on the benzimidazole groups. In other words, the capacitance increased with an increasing number of layers [20].

On the other hand, when all four imino N–H protons on the benzimidazole moieties were protected by N–Me groups, the capacitance decreased by 77% compared to that of the original PCET-type capacitor. This result strongly suggests that the proton movement plays a more important role than the anion movement in the charge storage. Furthermore, the proton movement accompanying the redox reaction in the Ru multilayer films on the ITO electrode was confirmed using a pH-indicator probe in aqueous solution. In this type of LbL films composed of Ru complexes that exhibit PCET-type redox reactions, the capacitance increases almost linearly with the number of layers (Figure 21) [20].

To obtain proton rocking-chair-type redox capacitors that use protons as the charge carriers, the quinone/hydroquinone couple is often used [52, 64–67]. However, at neutral pH, the electron–proton transfer rate of the quinone/hydroquinone couple is slower than that of the Ru(II/III) couple. The use of the LbL method to fabricate multilayered structures of redox-active Ru complexes that exhibit PCET is advantageous, as the storage capacity can be enhanced by increasing the number of redox-active modular units on demand.

3.5 Sequentially assembled heterolayer films of Ru complexes

One advantage of the LbL assembly method using metal coordination at the interface is that a combinatorial approach can be employed to construct sequentially ordered hetero-multilayer films (cf. Section 4.3).

Monolayer films of the Ru complexes 11 and 12 on ITO showed two well-defined CV waves at +0.83 and + 1.04 V and at −0.37 and + 0.09 V vs. Fc+/Fc, which were assigned to Ru(II)–Ru(II)/Ru(II)–Ru(III) and Ru(II)–Ru(III)/Ru(III)–Ru(III) processes, respectively. Due to the large differences between the potentials of 11 and 12, heterolayer films made from combinations of 11 and 12 exhibited interesting electronic/photon behaviors such as electron-transfer blocking, rectification, and vectorial photoelectron transfer. Figure 22 shows the CV responses of the heterolayer films ITO/(11)_n/(12)_m (n = 1, 2, where n stands for the number of layers) and ITO/(12)_n/(11)_m (n = 1, 3) and the alternating heterolayer films ITO/(11/12)_n, and ITO/(12/11)_n in CH₂CN (0.1 M HClO₄) [22, 62]. The ITO/(11)/12_1 bilayer hetero-film exhibited four waves (Figure 22a), which correspond to the redox processes from both the inner 11 and outer 12 layers; the Ru(II)–Ru(III)/Ru(III)–Ru(II) process of 11 and the Ru(III)–Ru(III)/Ru(III)–Ru(III) process of 12 overlap at +1.11 V. However, the peak separation of the outer layer of 12 increased at higher scan rates, while the peak separation for the waves from the inner layer of 11 remained unaffected. This result indicated a slower ET rate from the outer layer of 12 due to the higher spatial separation relative to the inner 11 film [22].

Conversely, for the ITO/(11/12)_2 hetero-film, in the first scan over the potential range of −0.5 V to +0.7 V vs. Fc+/Fc, only oxidative waves from 11 at +0.83 and + 1.04 V vs. Fc+/Fc were present; no waves from the outer 12 layer were observed (see blue line in Figure 22a). However, when the potential was scanned in the negative direction to −0.5 V, a large cathodic wave appeared at approximately −0.5 V vs. Fc+/Fc, and subsequently, a new anodic pre-peak at approximately +0.64 V (marked as x) was observed in the potential scan in the positive direction. The new pre-peak x was assigned as a catalytic oxidation wave derived from the ET of the outer 12 layers through ET mediation; that is, direct ET from the outer 12 layer to the electrode was blocked by the bilayer of 11, and an avalanche ET from
the outer 12 layers to the inner holes in 11 occurred through the potential gradient once a hole was generated in the inner 11 layers at the onset of the first 11 oxidation wave (Figure 23). Consequently, the large cathodic peak at \(-0.5\) V was assigned to the catalytic reduction wave of the 11 film mediated by the reduction process of the inner 11 film. Furthermore, the sequence of the 11 and 12 layers on the ITO electrode leads to characteristic CV responses depending on the sequence and the number of layers, as shown in Figure 22 [62].

Silicon-based \(pn\) heterojunctions play an important role in various types of electronic devices, such as diodes, transistors, solar cells and light-emitting diodes (LEDs). The potential difference at the \(pn\) junction causes blockage of charge transport, resulting in a rectification effect. Under photoirradiation, current flows through the external circuit, which acts as a silicon-based solar cell. Similarly, the photo-response of Ru-complex heterolayer films has been examined [22]. Photoirradiation of the ITO\((11)_{n}/(12)_{n}\) hetero-multilayer film in \(\text{CH}_3\text{CN} (0.1 \text{ M HClO}_4)\) at the open circuit potential of +0.45 V produced a cathodic photocurrent. The action spectrum of this film is nearly identical to the UV–vis absorption

\[
\text{Figure 22.}
\]

Cyclic voltammograms of heterolayer films of Ru complexes 11 and 12 with varying sequences: (a) ITO\((11)/12\)\(_n\) (\(n = 1, 2\), where \(n\) stands for the number of layers), (b) ITO\((12)/11\)\(_n\) (\(n = 1, 3\)), (c) alternating ITO\((11/12)\)\(_n\), and (d) ITO\((12/11)\)\(_n\) in \(\text{CH}_3\text{CN} (0.1 \text{ M HClO}_4)\) [22, 62].

\[
\text{Figure 23.}
\]

Rectified ET mechanism for the CV response of the ITO\((11)/12\)\(_n\) hetero-film shown in Figure 22a [22].
Spectrum of 11, which indicates the inner 11 layers are the main contributor to the photoexcitation, although little photo-response was observed for homo-Ru–complex multilayer films such as ITO|(11)_n or ITO|(12)_n. Interestingly, the direction of the photocurrent on the ITO|(11)_4/(12)_4 heterolayer film switched from cathodic to anodic after the application of a potential pulse at $-0.5\, \text{V}$. This photo-response change arose from the generation of a charge trapping state after the application of the pulse; the outer layers of 12 were reduced by the potential, and this reduced state was maintained as a charge-trapping state until holes were generated on the inner 11 layers by electrochemical oxidation or photoexcitation. This charge trapping state was recognized from the differential Vis–NIR spectra, in which a new inter-valence charge-transfer (IVCT) band at 1140 nm appeared for the mixed-valence state of 12 (Figure 24). Thus, the heterolayer film ITO|(11)_4/(12)_4 represents a typical example of a photo-responsive memory device; the writing process is achieved by applying a potential of either $-0.5$ or $+0.7\, \text{V}$, and the readout process is achieved by measuring the direction of the photocurrent [22]. Accordingly, the judicious selection of both redox potentials and the sequential ordering of the Ru modular units on the ITO surface makes it possible to design functional electronic devices such as molecular diodes and memory devices.

4. Molecular-device applications using Ru complexes on ITO

The idea of molecular devices is based on a next-generation paradigm to overcome the limitations associated with Moore’s law, which states that the number of transistors per silicon chip doubles every year, and the use of individual molecules as active electronic components. The first single molecular device was the theoretical proposal of a molecular diode by Aviram and Ratner; [68] subsequently, the concept of molecular electronic devices was further developed by Carter [69]. Various molecules have demonstrated basic electronic functionality as switches, as diodes for rectification, and as optical devices, storage devices, and sensing devices.
for future information technologies [54, 70]. The recent experimental development of single-molecular conductance measurements using metal–molecule–metal junctions [71] has opened a new avenue for the realization of molecular electronic devices through the judicious selection of molecules [70, 72–76]. Ru complexes are substitutionally inert in both the Ru(II) and Ru(III) oxidation states, and also exhibit fast self-exchange ET rates due to the small reorganization energy of the Ru (II/III) couple. Therefore, the use of a mixed-valence Ru(II)–Ru(III) complex as a perturbing motif branching from a conducting molecular wire has been proposed by Carter. Here, two molecular devices based on Ru complexes are discussed; the first is a Ru-complex molecular junction that exhibits rectification switching in response to humidity, and the other is a two-terminal memristor device based on the PCET reactions of Ru complexes.

4.1 Rectification switching in Ru complex molecular junctions in response to external humidity

Conductive-probe atomic force microscopy (C-AFM) was employed to measure the $I-V$ characteristics of self-assembled monolayers of Ru complexes on an ITO electrode. An ITO-coated Pt probe was used as the C-AFM tip in order to employ the same material for the top and bottom electrode, and the $I-V$ curves were measured via the two-terminal method [77].

Under dry (low humidity) conditions, the $I-V$ plots of both mononuclear 10 and dinuclear complex 11 became symmetric in the positive and negative potential range, indicating that the molecules at the junction behaved as a molecular wire or resistor (Figure 25). However, under the wet (high humidity) conditions, the $I-V$ curves became asymmetric and showed diode-like behavior only for dinuclear Ru complex 11, while they remained symmetric for 10. The rectification ratio $R = |I(-V)|/|I(V)|$ was found to have a high value of ~1000, where $|I(V)|$ represents the absolute value of the forward or reverse current density at a certain voltage. When the measurement conditions were changed from wet to dry, the $I-V$ plots for 11 became symmetric again. This rectification switching via humidity change occurred repeatedly for 11 (Figure 26); conversely, such switching was not observed for 10 [77].

Figure 25.
Structures of Ru complexes 10 (top) and 11 (bottom), log $I-V$ curves of the 10 and 11 molecular junctions under low humidity (5%) and high humidity (60%) conditions, and 2D histograms of the rectification ratio (R) at high humidity [77].
Several factors need to be considered to explain this behavior. The tip-radius affected the asymmetry of the $I$–$V$ curves, whereby a small tip (50 nm radius) leading to a larger rectification ratio $R$ on account that water molecules were more strongly attracted to the smaller tip. However, this effect could not fully explain the absence of asymmetry for 10. Based on combined theoretical and experimental results, water molecules and counter-ion displacement have an important influence on two localized molecular orbitals in 11, and under an applied voltage bias, a large asymmetry was induced externally via water molecules screening the counter-ions. Thus, via these rectifying properties, the self-assembled Ru complex 11 molecular junctions act as nanoscale sensors with ON/OFF switching in response to external humidity [77].

4.2 Protonic memristor devices based on Ru complexes with PCET

Recently, memristors have attracted substantial attention as the fourth passive element after resistors, capacitors, and inductors. The memristor was predicted by Chua in 1971 as a new electronic circuit element linking charge and magnetic flux, [79] and the first example of such a device was demonstrated experimentally in 2008. This first memristor device consisted of TiO$_2$$_{2-x}$ sandwiched between two Pt metal terminals, in which the oxygen defects led to filament formation, and the defects acted as mobile charged dopants and drifted in the applied electric field [80]. As a result, the device exhibited a periodic pinched hysteresis loop in its $I$–$V$ curves. Since then, not only metal oxides, but also many other materials such as organic polymers and metal chalcogenide films, have been sandwiched between the two terminals to fabricate devices with a non-linear hysteretic $I$–$V$ loop [81, 82]. In the two-terminal devices, non-linear changes in the current occur during the voltage sweep, and the associated resistance changes. This type of electric element is generally referred to as a memristor. In recent years, the memristor has become relevant in the context of the action of synapses in the neuromorphic systems of the brain. In biological synapses, ion/molecule migration is used for signal transduction. Inspired by the ion migration in the synapse system, we developed a system in which a proton serves as the charge carrier at the interface between Ru complexes with PCET properties and a proton-conducting polymer such as poly(4-vinylpyridine) (P4VP). In Section 4.4.3, a charge-storage system was constructed from two electrodes modified with films of the Ru complexes 16 and 17, which show PCET properties in unbuffered 0.1 M NaClO$_4$ solution, and the resulting two-terminal cells showed a stable charging–discharging process via a proton rocking-chair-type mechanism. The unbuffered aqueous solution was replaced with
proton-conducting P4VP (pK$_a$ ~ 4.0–5.2), and the resulting two-terminal heterolayer device, ITO(16) /P4VP/(17) /ITO, was tested. Figure 27 shows the typical I–V characteristics of the two-terminal device, which produced “8” shaped and non-linear I–V loop curves [83].

To elucidate the coupling of the proton-transfer ability of P4VP and the PCET reactions of Ru complexes 16 and 17 at the hetero-interface, CV measurements were performed in 0.1 M NaClO$_4$ aqueous solution (Figure 28). A large negative potential shift was observed for the Ru(II/III) peak of the ITO(16) /P4VP film compared to that of ITO(16) without P4VP. This negative potential shift arises from the hydrogen-bonding interactions between the N–H benzimidazolyl groups in 16 and the pyridine groups in P4VP, based on a previous study of the hydrogen-bonding interactions between the N–H imino groups in Ru–benzimidazole-derivative complexes and N-heteroaromatics such as pyridine [84]. In this study, the magnitude of the shift was strongly correlated to the pK$_a$ values of both components (i.e., the complex and the heteroaromatic component) [84]. On the other hand, only a small potential shift was observed between the peak of the ITO(17) /P4VP film and that of ITO(17) without P4VP. The difference between these two systems was attributed to the pK$_a$ difference between the Ru complexes in the Ru(II) and Ru(III) oxidation states.

Figure 27.
I–V plots of the two-terminal device ITO(16) /P4VP/(17) /ITO, showing ten scans on the same device. The blue line indicates the average of the ten scans [83].

Figure 28.
Cyclic voltammograms of ITO(16) /P4VP (blue solid lines) and ITO(17) /P4VP films (red solid lines), together with those of ITO(16) (blue dotted lines) and ITO(17) films (red dotted lines), in 0.1 M NaClO$_4$ aqueous solution, as well as a schematic illustration of the hydrogen-bonding interactions between the Ru complex 16 and the P4VP polymer [83].
In the initial stage, the 16 site of the two terminal device ITO[(16)/P4VP/(17)]3 is in the Ru(II) oxidation state with pKa values in the range of 4.1–8.8, while the 17 site on the other side is in the Ru(III) state with pKa values in the range of 5.2–9.8. The pKa value of the intervening P4VP polymer is 4.0–5.2. Thus, the proton gradient across the interfaces is small, and it is equilibrated through hydrogen bonding between the P4VP and both 16 and 17 (Figure 29). When a bias potential of +1.5 V is applied to the two-terminal ITO[(16)/P4VP/(17)]3|ITO device, redox processes occur on the immobilized Ru complexes, namely, the oxidation of 16 from the Ru (II) state to Ru(III) takes place at the positive-potential side of the terminal, accompanied by the reduction of 17 from the Ru(III) state to Ru(II) at the other terminal. The resulting redox reactions induce large changes in the pKas of 16 and 17 relative to those of their initial Ru(II) or Ru(III) states, resulting in a large proton gradient across the immobilized Ru complex/P4VP interfaces (Figure 11). Specifically, the pKa of 16 drops to <3.8, which means that protons are easily released upon the oxidation of 16, while on the 17 side, the pKa increases to >8.4. Given the pKa value of the intervening P4VP is 4.0–5.2, the (16)/P4VP proton transfer equilibrium is shifted toward the protonation of the P4VP side, while at the (17)/P4VP side, the equilibrium shifts toward the protonation of the film of 17 upon reduction of the Ru center. The proton conductivity through the protonated P4VP layer is improved by the resulting large pKa gradient, resulting in enhanced conduction until the opposite redox reactions take place at both terminals. When the bias potential was scanned in the negative direction toward −1.5 V, the pKa gradient returned to the initial state, and the current decreased in the absence of a driving force for electron or proton transport between 16/P4VP and P4VP/17.

Therefore, the large pKa difference in the Ru complexes 16 and 17 induced by the PCET redox reactions at the two terminals cause a proton gradient across the intervening proton-conducting P4VP, leading to high proton conductivity under an applied voltage. The change in the proton gradient due to the PCET redox reaction in the two-terminal device can be applied to use the proton-conducting switching devices as protonic memristors [83].

Figure 29.
Schematic illustration of the proton-conduction switching in the two-terminal device ITO[(16)/P4VP/(17)]3|ITO and the pKa gradient under the applied positive bias potential. The numbers refer to the pKa values of the Ru(II) and Ru(III) complexes [83].
5. Miscellaneous devices based on Ru–benzimidazole complexes for solar-energy transduction

Further important applications for ruthenium complexes include photoredox catalysts and dye-sensitized solar cells. In particular, Ru(bpy)$_3$ or Ru(tpy)$_2$ derivatives have been used as photosensitizer dyes on mesoporous TiO$_2$ surfaces in Grätzel-type solar cells. Over the past two decades, many Ru complexes with phosphonate anchors have been reported, [33] and many Ru dyes derived from Ru(bpy)$_3$ derivatives that contain phosphonate anchors (Figure 30). Additionally, Ru-2,6-bis(benzimidazole-2-yl)pyridine complexes have been employed as photoredox catalysts [85, 86]. The Ru–benzimidazole bond is known to be more stable than the Ru–pyridine bond in the photoexcited state, rendering such Ru-benzimidazole complexes promising candidates for photoelectrochemical redox catalysts.

6. Conclusion

Substitutionally inert ruthenium complexes bearing benzimidazole derivatives have unique electrochemical and photochemical properties. In particular, proton-coupled electron-transfer in ruthenium–benzimidazole complexes endows them with rich redox chemistry and makes them useful as a modular unit for redox mediators or reactive sites for switching by external stimuli. In this chapter, the role of PCET reactions on Ru–benzimidazole complexes in energy-storage applications and the tuning of metal–metal interactions in aqueous solution was emphasized first. Based on this knowledge acquired from solution chemistry, the chemistry of Ru complexes confined on an electrode surface via their self-assembling from solution for the fabrication of the surface functional molecular devices on electrodes was discussed. Indium-tin oxide (ITO) is often chosen as the electrode due to its transparency and wide use as a substrate in electronics. To immobilize the redox-active Ru complexes on an ITO electrode, tetrapod phosphonic acid anchor groups...
are often incorporated into tridentate 2,6-bis(benzimidazole-2-yl)pyridine or ben-
zene ligands, which enables the construction of free-standing self-assembled
monolayer structures on an ITO electrode. Starting from this monolayer as a primer
layer, multilayer films can be constructed by the LbL layer growth method. The
resulting multilayers using redox-active Ru complexes as a modular unit exhibited
long-range electron transport even in films with over 60 layers (~100 nm thick)
through the “stepping-stone” mechanism. Furthermore, a combinatorial approach
to LbL layer growth can be used to obtain bespoke functional heterolayer films via
material design. Using this strategy, blocking of electron transfer or rectification
can be made to occur in such Ru complex heterolayer films, which results in charge
trapping; the trapped electrons can subsequently be released via photo-irradiation,
which leads to the new concept of photo-responsive memory devices. The CV
response of multilayer films of Ru complexes with PCET depends strongly on the
pH value. By judicious selection of the redox potentials and pKₐ values of the two Ru
complexes with PCET properties, two-electrode cells based on the Ru complex
multilayer films that acted as proton rocking-chair-type redox capacitors can be
obtained. Furthermore, by sandwiching a proton-conducting polymer between two
Ru multilayer terminals, new type of protonic memristor device can be fabricated.

Therefore, surface-confined Ru complexes exhibit highly promising potential
for the development of new functional molecular-based devices.

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Dedication

This chapter is dedicated to my good friend Prof. Wolfgang Kaim on the occa-
sion of his 70th birthday, and to my late wife, Masako Haga, who has supported my
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