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Nanometric Assembly of Functional Terpyridyl Complexes on Transparent and Conductive Oxide Substrates: Structure, Properties, and Applications

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CONSPECTUS: Over the last few decades, molecular assemblies on solid substrates have become increasingly popular, challenging the traditional systems and materials in terms of better control over molecular structure and function at the nanoscale. A variety of such assemblies with high complexity and adjustable properties was generated on the basis of organic, inorganic, organometallic, polymeric, and biomolecular building blocks. Particular versatile elements in this context are terpyridyls due to their wide design flexibility, ease of functionalization, and ability to coordinate to a broad variety of transition-metal ions without forming diastereoisomers, which facilitates tuning of their optical and electronic properties. Specifically, metal–terpyridyl complexes are worthy building blocks for generating optoelectronically active assemblies on technologically relevant transparent and conductive oxide substrates.

In this context, the present Account summarizes our recent results on the preparation, characterization, and applications of nanometric (2–10 nm) surface-confined molecular assemblies of Cu²⁺, Fe²⁺, Ru²⁺, and Os²⁺–terpyridyl complexes on SiO_x-based substrates (glass, quartz, silicon, and ITO-coated glass). These assemblies rely on covalent bond formation between the iodo-/chloro-terminated functionalized SiO_x substrates and the pendant group (mostly pyridyl) hosted on the terpyridyl complexes. Such an anchoring provides excellent thermal, temporal, radiative, and electrochemical stability to the assemblies as needed for technological applications. The functional, covalently assembled monolayers were extended to fabricate molecular dyads (bilayers), triads (trilayers), and oligomers by an established layer-by-layer procedure using suitable metallolinkers such as Cu²⁺, Ag⁺, and Pd²⁺. The chemical, optical, and electrochemical properties of these assemblies could be precisely adjusted by selection of proper metal–terpyridyl complexes and/or metallolinkers, so that the resulting systems served, relying on the specific design, as sensors, catalysts, molecular logic gates, and photochromic devices. For instance, a Cu–terpyridyl-based assembly on a glass substrate showed “turn on” detection of ascorbic acid. In another example, heterometallic molecular triads were exposed to redox-active NO⁺ for selective oxidation of the metal ions, and the optical readout was utilized for configuring multiple-input-based molecular logic gates. Furthermore, bias-driven (+0.6 to +1.6 V vs Ag/AgCl) optical properties of the heteroleptic Ru²⁺/Os²⁺–terpyridyl monolayers were modulated and “read out” by spectro-electrochemical techniques demonstrating high charge/information density (3–4 × 10¹⁴ electrons/cm²). Moreover, the manipulation of the M^{2+/3+} (M = Fe, Ru, and Os) redox wave in the assembly provided the possibility to create mixed-valence redox-states paving the way toward the fabrication of “multi-bit” memory systems. We truly believe that due to these intriguing characteristics and excellent stability, terpyridyl-based molecular assemblies have the potential to become a versatile platform for the next generation of smart optoelectronic devices.

INTRODUCTION

Nanometric molecular assemblies fabricated on solid supports, including technologically relevant optically transparent and conductive substrates, are important elements of modern nanotechnology and related applications.^{1,2} Upon such an assembly, uncontrolled motion and orientation of functional molecules, which is typical in solution, can be avoided, making a system operational for practical purposes.^{3–6} In addition, such surface-confined systems represent an attractive platform for “proof-of-principle” studies, for they offer a high degree of

molecular control through dense and aligned molecular packing.⁷

Within the general concept of surface-confined systems, the highest degree of integrity is typically achieved by fabrication of monomolecular layers, relying on self-assembly and covalent bond formation between the substrate and functional molecules. The constituents of such monolayers contain a

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Scheme 1. (a) Schematic of Fabrication of Covalently Assembled Monolayers on SiO_x Substrates^{II} (b) Schematic of LbL Deposition Method for Preparing Dyad, Triad, and Oligomer Assemblies^{III}

^{II}(A) Cleaning and thermal activation of substrates. (B) Assembly, cleaning, and activation of silane-coupling layer (CL). (C) Attachment of functional terpyridyl complexes to CL. ^{III}At first, metalloligands (blue rods) are attached to CL (black rods) resulting in the formation of the monolayer, serving as a template layer for the subsequent growth. Afterwards, repetitive chemical reactions between the assembled metalloligands and those in solution, mediated by “intermediate” metallolinkers (red circles), lead to the formation of the desired assembly.

substrate-specific anchoring group, a backbone (spacer), and a terminal (tail) group, with all of these units serving a specific purpose.⁷ Within this general architecture, functional terpyridyl complexes on transparent and conductive oxide substrates represent particularly promising systems, for they offer numerous advantages including: (i) facile synthesis of terpyridyl derivatives and their metal complexes (achiral and isomer-free); (ii) easy functionalization (as compared, e.g., to the established bipyridyl complexes);^{8–11} (iii) robust structure due to the comparably strong metal-to-ligand back bonding [$d\pi(\text{M})-\pi\pi(\text{L})$]; (iv) versatile coordination modes; (v) tunable and reversible redox properties; (vi) tunable metal-to-ligand charge-transfer (MLCT) bands in the entire visible region; (vii) the possibility to extend monolayers to oligomeric assemblies.¹²

Keeping these considerations in mind, in this Account, we review our recent results on the fabrication of nanometric assemblies of terpyridyl complexes on transparent and conductive oxide substrates, their detailed characterization, optoelectronic properties, and applications in catalysis, sensing, molecular logic, and data storage.

■ FABRICATION OF NANOMETRIC COORDINATION-BASED FILMS VIA LAYER-BY-LAYER ASSEMBLY

Among different substrates for molecular thin films, SiO_x -based supports, such as glass, quartz, single-crystal silicon, and indium tin oxide (ITO)-coated glass, are of particular importance due to their well-defined surface attributes, extensive applications in the microelectronic industry, low cost, ease and reproducibility of surface modification, straightforward characterization, and applicability for optical, electrical, and optoelectronic addressing and readout. We relied on silane-based compounds from a broad variety of coupling agents, which included carboxylate, amine, pyridyl, azide, and phosphonate, to couple functional

terpyridyl complexes to SiO_x substrates. The procedure to prepare functional monolayers involved three basic steps as shown in Scheme 1a, viz. substrate activation, its silanization, and attachment of metal–terpyridyl coordination complexes using a substitution nucleophilic reaction ($\text{S}_{\text{N}}2$).¹³ Such complexes provide a high degree of structural diversity, including flexible geometry, and variable coordination modes between the metal ions and organic ligands. The respective metal–organic linker interactions can be utilized for the fabrication of ordered multilayer assemblies by layer-by-layer (LbL) deposition method, with reliable control over the growth mode through smart design of the building blocks.^{14–18} Through the use of functionalized molecular units, surface-confined materials with layered architectures and enhanced molecular properties can be prepared,^{19,20} including heterometallic systems which might be useful for multibit data storage. Following this general approach, we employed the LbL process for growing dyad, triad, and oligomer films, using functional, pyridyl-terminated terpyridyl complexes (metallo-ligands) and inorganic (metallo-linkers) or organic coupling units as their building blocks (Scheme 1b).

■ STRUCTURAL, OPTICAL, AND REDOX PROPERTIES OF SURFACE-CONFINED MOLECULAR DYADS AND TRIADS

Metal-ion-controlled heterometallic dyads were prepared on SiO_x substrates by employing the wet-chemical LbL deposition process. At first, the substrates were chemically functionalized by 3-iodo-*n*-propyltrimethoxy-silane as the CL. Afterward, covalently assembled monolayers (termed as the template layers) of metal–terpyridyl complexes (abbreviated as MPT, with $\text{M} = \text{Fe}^{2+}$, Ru^{2+} , and Os^{2+} ; PT = 4′(4-pyridyl)[2,2′:6′,2″-terpyridine], and two PT units involved in each MPT complex) were formed via $\text{S}_{\text{N}}2$ reaction between the pyridyl and iodo-

terminated CL. Finally, the second complex was connected to the template layer over a Cu^{2+} metallolinker (Scheme 2).²¹

Scheme 2. Schematic of the Heterometallic Molecular Dyads Formed on SiO_x Substrates Using the Cu^{2+} Metallolinkers[⊥]

[⊥](a) FePT/Cu/RuPT; (b) RuPT/Cu/OsPT; (c) OsPT/Cu/FePT.

The resulting molecular dyad films ($\text{SiO}_x/\text{M}_1\text{PT}/\text{Cu}^{2+}/\text{M}_2\text{PT}$) were ~ 3 nm thick and had an average tilt angle of $\sim 30^\circ$ with respect to the surface normal. Significantly, these films showed merged optical and electrochemical signatures of the involved metalloligands. For example, the UV–vis spectrum of the FePT/Cu/RuPT layer exhibited the ¹MLCT bands of RuPT and FePT ($d\pi$ ($\text{M} = \text{Fe}, \text{Ru}$)- π^* (PT) processes) at $\lambda_{\text{max}} = 502$ and 605 nm, respectively (Figure 1a). For the RuPT/Cu/OsPT layer, a strong ¹MLCT band at $\lambda_{\text{max}} = 502$ nm represented a merged response of both metalloligands, along with the weaker ³MLCT band associated with Os^{2+} (Figure 1b). Similarly, the OsPT/Cu/FePT film showed three different MLCT transitions in the visible region corresponding to the assembled metalloligands (Figure 1c). Importantly, the MLCT bands of the dyad films showed clear blue shifts (up to 25 nm,²¹ which is much larger than those for the oligomer films; vide infra²²) as compared to the respective monolayers, which can be partly ascribed to intramolecular electronic communication across the layer mediated by the metallolinkers, along with the possible effect of H-type aggregations. Such a communication could also be tracked in cyclic voltammograms (CVs) of the FePT/Cu/RuPT and RuPT/Cu/OsPT dyad layers, where Cu^{2+} -mediated electron-density transfer led to comparably low potential for the single-electron oxidation processes with a

difference between the involved metal ions of ~ 250 mV ($\Delta E = E^{\text{Ru}^{2+/3+}} - E^{\text{Fe}^{2+/3+}}$) and ~ 350 mV ($\Delta E = E^{\text{Ru}^{2+/3+}} - E^{\text{Os}^{2+/3+}}$), respectively (Figure 2a,b). The reversible, outer-sphere redox processes ($\text{M}^{2+/3+}$), specific for each involved metalloligand, were well traceable for the dyad layers, while differences in the oxidation potentials might be useful for multibit charge storage, with an estimated charge density of $7.5\text{--}15 \times 10^{13}$ electrons/ cm^2 at the given density of the metalloligands. In contrast, the OsPT/Cu/FePT system has one-bit storage capability, since both the redox peaks of both metalloligands overlap in the range of $+(0.85\text{--}1)$ V (Figure 2c).

As a further step, metallolinker (Cu^{2+})-mediated heterometallic molecular triad layers comprising three different metalloligands (FePT, RuPT, OsPT) were fabricated with a quite high efficiency of coordination ($80 \pm 3\%$), as estimated by the UV–vis data.²³ A combination of three different metalloligands with well-separated redox signals in one functional moiety provides a possibility of even more advanced multibit data storage.²⁴ As an example of basic characterization, we present here the C and N K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra illustrating the assembly of the FePT/Cu/RuPT/Cu/OsPT triad layer (Scheme 3a). While, at the C K-edge, a weak, pre-edge π^* resonance (0) at ~ 285.2 eV was observed for the iodo-silane containing CL, the FePT to triad layers exhibited strong resonances at ~ 284.9 and ~ 285.7 eV (1) as shown in Figure 3a. In addition, the latter layers displayed strong π^* resonance at $399.6\text{--}399.8$ eV (1) at the N K-edge, as a clear fingerprint of the pyridine and terpyridine units (Figure 3b). Remarkably, additional strong resonance was observed at ~ 405.7 eV (2) for the Cu-terminated layers (for example, FePT/Cu), assigned to NO_3^- counterions strongly attached to the Cu^{2+} ions. The average tilt angle of the metalloligands was estimated at $\sim 35^\circ \pm 3^\circ$, in good agreement with the value deduced from ellipsometry measurements.

The UV–vis spectra of the triad layers represent a superposition of the spectra of the involved metalloligands, with the respective ¹MLCT bands being well perceptible and the optical windows of the triad films covering the entire visible region (Figure 4). In addition, the ¹MLCT bands of the assembled metalloligands exhibit distinct shifts in the band maxima and also exhibit band broadening,²³ which, similar to the dyad case, can be partly attributed to intramolecular

Figure 1. UV–vis absorption spectra of the template (green), Cu^{2+} -terminated template (red) layers, and heterometallic dyads (blue) on glass substrates. (a) FePT (i), FePT/Cu (ii), and FePT/Cu/RuPT (iii); (b) RuPT (i), RuPT/Cu (ii), and RuPT/Cu/OsPT (iii); (c) OsPT (i), OsPT/Cu (ii), and OsPT/Cu/FePT (iii). The black lines (iv) represent the spectra of the glass substrate (“baseline”). Reproduced with permission from ref 21. Copyright 2013 Wiley.

Figure 2. CVs of the template layers (black) and heterometallic molecular dyads (red) on ITO-coated glass substrates. (a) FePT and FePT/Cu/RuPT layers: (i) and (ii) $\text{Fe}^{2+/3+}$, (iii) $\text{Ru}^{2+/3+}$; (b) RuPT and RuPT/Cu/OsPT layers: (i) $\text{Ru}^{2+/3+}$, (ii) $\text{Os}^{2+/3+}$, and (iii) $\text{Ru}^{2+/3+}$; (c) OsPT and OsPT/Cu/FePT layers: (i) $\text{Os}^{2+/3+}$, (ii) and (iii) merging of $\text{Fe}^{2+/3+}$ and $\text{Os}^{2+/3+}$ redox processes. Reproduced with permission from ref 21. Copyright 2013 Wiley.

Scheme 3. Schematic of Heterometallic Molecular Triads Formed on SiO_x Substrates Using the Cu^{2+} Metallolinkers[#]

[#](a) FePT/Cu/RuPT/Cu/OsPT, (b) FePT/Cu/OsPT/Cu/RuPT, (c) RuPT/Cu/OsPT/Cu/FePT, and (d) OsPT/Cu/RuPT/Cu/FePT.

Figure 3. C (a) and N (b) K-edge NEXAFS spectra of the coupling (CL), template (FePT), template-Cu, dyad, dyad-Cu, and triad layers for the FePT/Cu/RuPT/Cu/OsPT assembly on Si(100). The spectra were acquired at an X-ray incidence angle of 55° (magic angle; no effects of molecular orientation). Reproduced with permission from ref 23. Copyright 2015 American Chemical Society.

electronic communication between the individual MPT units linked with Cu^{2+} .

CVs of the triad layers fabricated on ITO-coated glass also showed shifts of 60–70 mV in the redox potentials with respect to the template and dyad layers due to the transfer of electron density between the individual metallolinkers (Figure 5). Thus, intramolecular electronic communication facilitated by a conductive inorganic coupling unit (Cu^{2+}) seems to be quite efficient, which can be useful for nanoscale electronic

applications.²⁵ Additionally, there are also some features at lower potentials (+0.5 to +0.6 V) that are most likely related to the formation of a mixed-valence redox species which are not prominent in the dyad assemblies.

The reduced and oxidized states of the individual metal centers in the heterometallic triads can be set equivalent to the “0” and “1” states, respectively. The available redox states in the triad layers can then be expressed as “000” (all metal centers are nonoxidized, <0.3 V), “100” (one metal center is oxidized at +0.6 V), “110” (two metal centers are oxidized, at 1.2 V), and “111” (all metal centers are oxidized at >1.42 V), resulting in a multibit data storage. Note that the well-distinguished MLCT bands and redox behavior of individual MPT units were employed as specific sensing attributes to design molecular logic gates (see below).

■ SURFACE-CONFINED MULTICOMPONENT OLIGOMER FILMS

Along with the dyad and triad layers, oligomeric films were fabricated employing LBL assembly of the terpyridyl complexes.^{22,26} These films contained either repeating RuPT units²² or alternating RuPT and OsPT units²⁶ coupled with Cu^{2+} , Pd^{2+} , Ag^+ , Fe^{2+} , Co^{2+} , or Zn^{2+} metallolinkers in zigzag fashion (Scheme 4). The optical properties of the respective assemblies depended strongly on the selection of linker. For example, there was continuous blue shift of the MLCT band of RuPT for the Cu^{2+} -based assembly from $\lambda_{\text{max}} = 498$ nm for the RuPT template layer to $\lambda_{\text{max}} = 479$ nm for the 9-fold oligomer film.²² However, when Cu^{2+} (d^9 electronic state) was replaced by Ag^+ (d^{10} electronic state), no substantial change in the position of the MLCT band was observed,²² which suggests that UV–vis spectral shifts can be indeed associated with

Figure 4. UV-vis spectra of the FePT/Cu/RuPT/Cu/OsPT (a), Fe-PT/Cu/OsPT/Cu/RuPT (b), RuPT/Cu/OsPT/Cu/FePT (c), and OsPT/Cu/RuPT/Cu/FePT (d) triad films as well as respective template and dyad layers on glass substrates. Black, red, blue, and purple solid lines represent the spectra of the glass substrate (“baseline”) and the template, dyad, and triad layers, respectively. Reproduced with permission from ref 23. Copyright 2015 American Chemical Society.

Figure 5. CVs of the RuPT, RuPT/Cu/FePT, and RuPT/Cu/FePT/Cu/OsPT layers (a), OsPT, OsPT/Cu/FePT, and OsPT/Cu/FePT/Cu/RuPT layers (b), and OsPT, OsPT/Cu/RuPT, and OsPT/Cu/RuPT/Cu/FePT layers (c) on ITO-coated glass substrates. Red, blue, and purple solid lines are the voltammograms of the corresponding template, dyad, and triad layers, respectively. Reproduced with permission from ref 23. Copyright 2015 American Chemical Society.

intramolecular electronic communication rather than with H-aggregation effects. For the surface-confined, coordination-based diblock oligomers (SURCOs), exhibiting a merged, superimposed MLCT band at $\lambda_{\text{max}} = 501\text{--}503\text{ nm}$ (Figure 6), the effect of the linker was even stronger. The Cu^{2+} -linked oligomer film (SURCO-1) showed linear film growth with each coordination step, with a square pyramidal geometry in the layered structure and the *trans* positioning of two pendant pyridyl groups. In contrast, the Pd^{2+} -linked film (SURCO-2) exhibited an exponential growth, with a square-planar spatial arrangement of Pd^{2+} in the lattice and a specific (“in-and-out movement”²⁷ of Pd^{2+}) growth mechanism. Note that the MLCT band shifts were pronounced in the SURCOs when

$\text{Cu}^{2+}/\text{Pd}^{2+}$ were used as linkers but not for other transition-metal ions, which negates the contribution of the aggregation effects. Note also that the linear growth of both homonuclear and diblock oligomer films probably has some limits because of possible distortions and polar angle inclinations; even macrocyclization is possible for analogous systems in certain cases.^{28–30} The exact structure of the oligomer films is an important issue as well, with the possible random orientations of the ligands, proposed zigzag arrangement of the individual complexes,^{22,26,31} or even possible, crystalline structure of the assemblies.³²

Scheme 4. Schematic of the SURCO Films Prepared via LbL Assembly Method with Alternative Use of the RuPT and OsPT Units and Either Cu^{2+} (SURCO-1) or Pd^{2+} (SURCO-2) Metallolinkers

■ APPLICATIONS OF THE METALLOTERPYRIDYL ASSEMBLIES

Flexible design of metal–terpyridyl complexes and related assemblies allows for a variety of potential applications as will be demonstrated below by the example of several representative model systems, which can only be considered as prototypes of real devices. Other applications, mentioned below in this section and in [Concluding Remarks](#), are possible as well, on the basis of both metal–terpyridyl moieties and analogous metallo-organic complexes.

Cu–Terpyridyl Monolayer for Sensing Ascorbic Acid

Monolayer-based sensor systems are, in general, based on relatively weak but selective and reversible noncovalent host–guest interactions. In contrast, we employed a nondestructive, solution-to-surface one-electron transfer process for “turn-on” optical-sensing of 0.5–5.5 ppm of ascorbic acid (AA; Vitamin C) in water, with a detection limit of (<0.5 ppm) using a five-coordinated Cu^{2+} complex such as a PT–Cu–(OAc)₂ monolayer (OAc = acetate) assembled on a glass substrate.³³ Notably, AA is an important biomolecule required for healthy body activity and, therefore, is of high significance in diagnostics. Exposure of this redox-active film to 0.5 ppm of aqueous AA promoted conformational change from d^9 - Cu^{2+} square pyramidal to d^{10} - Cu^+ tetrahedral geometry, accompanied by the appearance of a new MLCT band ($\lambda_{\text{max}} = 423 \text{ nm}$) attributed to the Cu^+ state (Figure 7a). At the same time, when two acetate ions were replaced by a rigid, bidentate chelate ligand (1,10-phenanthroline (phen)) no such spectral changes were observed (Figure 7b) confirming the proposed mechanism of the electron-transfer reaction mediated by the movement of the labile acetate moiety and accompanied by the rotation/bending (up to 15°) of the pyridyl ligand.

Cu–Terpyridyl Monolayer for Catalytic Activity

The PT–Cu–(OAc)₂ monolayer could also be employed for catalytic oxidation of AA with high turnover number and frequency.³⁴ Within this process, AA dissociated reversibly to its monoionic form (ascorbate anion), which was the rate-determining step. Subsequently, ascorbate anion started a series of reactions by coordinating to Cu^{2+} in the PT–Cu–(OAc)₂ film (Figure 8), which eventually led to the AA oxidation to dehydroascorbic acid (DHA), signified by gradual decrease in AA absorbance at $\lambda_{\text{max}} = 264 \text{ nm}$ (Figure 8). Additionally, we also investigated the photonuclease activity of Cu^{2+} -based molecular films.³⁵

Figure 6. UV–vis spectra of SURCO-1 (a) and SURCO-2 (d) on glass substrates (see Figure 5). The absorbance at λ_{max} for SURCO-1 (b) and SURCO-2 (e) as functions of the oligomer chain length, with the curves being fitted by either linear (b) or exponential (e) functions. The relations between absorbance and density of the metalloligands (metalloligands/ cm^2) for SURCO-1 (c) and SURCO-2 (f). Reproduced with permission from ref 26. Copyright 2015 American Chemical Society.

Figure 7. UV-vis absorption spectra of the (a) PT-Cu-(OAc)₂- and (b) PT-Cu-(1,10-phen)-based monolayers on quartz substrate: (i) undisturbed monolayer, (ii) after exposing to ascorbic acid (5.5 ppm), (iii) recovered monolayer, and (iv) baseline. The gray and pink shaded areas represent the oxidized and reduced films, respectively. Top inset in (a) shows the one-electron redox process (Cu²⁺/Cu⁺) with AA as the reducing agent and air/O₂ as the oxidizing agents. Top inset in (b) illustrates a lack of AA-induced electron transfer for the PT-Cu-(1,10-phen) case. Bottom insets show the chemical structures of the monolayers. Reproduced with permission from ref 33. Copyright 2012 Royal Society of Chemistry.

Figure 8. Left panel: UV-vis absorption spectra of AA in water (150 μM) exposed to PT-Cu-(OAc)₂ film on quartz. The spectra were recorded from the beginning of the reaction ($t = 0$; top curve; thick black line) to $t = 4$ h (bottom curve; thick black line). Right panel: proposed mechanism for electron-transfer-based oxidation of AA. Adapted with permission from ref 34. Copyright 2014 Royal Society of Chemistry.

Detection of NO⁺ and Boolean Logic Gates on the Basis of the Triad Assemblies

Detection of the redox-active, water-sensitive cation NO⁺, particularly in organic solvents, is significant in terms of elucidating reaction mechanisms; it is involved in many inorganic, organometallic, and organic reactions as an intermediate or an important component in reaction pathways.³⁶ Additionally, such entities often act as external chemical triggers, either in solution or solid phase, for altering molecular properties to yield multiple, different molecular states leading to molecular switches and allowing them to create molecular logic via a bottom-up approach, thereby, mimicking Boolean logic.³⁷ The latter is particularly interesting in view of its emerging applications including as a photosensitizer³⁸ and its involvement in paper-based molecular logic as well as other endeavors.³⁹ We tested the OsPT/Cu/RuPT/Cu/FePT triad film in this context. A 30 s exposure of this film to ppm levels of NOBF₄ led to a bathochromic shift of the MLCT band of the FePT unit ($\lambda_{\text{max}} = 577$ nm) by ~19 nm, along with $60 \pm 2\%$ decrease in absorbance (Figure 9a),²³ attributed to the quaternization/oxidation of the terminal pyridyl group by NO⁺ and subsequent oxidation of Fe²⁺ to Fe³⁺. Additionally, the merged ¹MLCT band of the RuPT and OsPT units ($\lambda_{\text{max}} =$

Figure 9. (a) Ex situ UV-vis spectra of OsPT/Cu/RuPT/Cu/FePT triad layer before and after exposure to 100 ppm of NOBF₄ (release of NO⁺) in dry acetonitrile for different times (marked at the curves), and (b) absorbance of the most prominent MLCT bands (λ_{max} at 508, 577, and 690 nm) versus the exposure time. Reproduced with permission from ref 23. Copyright 2015 American Chemical Society.

508 nm) was blue-shifted by ~7 nm, followed by a substantial decrease in absorbance. However, full oxidation of the metal centers, involving also Os²⁺, could only occur after 10 min of NOBF₄ exposure (Figure 9b). Such a delay, in spite of the lower oxidation potential of Os²⁺ as compared to that of Fe²⁺, was ascribed to the strong quaternization of the terminal

Scheme 5. Proposed Mechanism of Oxidation/Reduction and Quaternization/Dequaternization of the OsPT/Cu/RuPT/Cu/FePT Triads on Glass Substrates ∇ , $\circ$

∇ (a) Neutral form; (b) quaternized (topmost pyridyl moiety) and partly oxidized (Fe^{3+}) form upon reaction (30 s) with 100 ppm of NO^+ , and (c) quaternized-oxidized form (Os^{3+} , Fe^{3+}) upon a prolonged (10 min) exposure to NO^+ . $\circ$ The oxidized states of the FePT and OsPT units are marked by light pink and red, respectively. The reaction can be reversed by subsequent use of H_2O and Et_3N .

pyridyl group by NO^+ . As a result, the Fe center in the topmost unit of the triad experienced an electron-withdrawing effect which did not occur for the Os center (bottom unit). At the same time, the Ru^{2+} center remained unoxidized due to its high oxidation potential. Significantly, the initial spectrum of the triad layer could be reset by subsequent application of H_2O and Et_3N (Scheme 5).

The selective and reversible changes in the triad layer by the input of NO^+ , accompanied by the changes in the UV-vis spectra forming an interpretable output, provide a basis for creation of complex Boolean logic. For instance, combinatorial molecular logic gate(s) can be designed by application of NO^+ , H_2O , and Et_3N to the OsPT/Cu/RuPT/Cu/FePT triad layer as three separate chemical inputs, In1, In2, and In3 ("1" when applied, "0" otherwise) and considering changes in absorbance at 577 and 501 nm as possible outputs ("0" for no change - "OFF" state and "1" for a certain change - "ON" state). For example, upon exposure of the triad layer to NO^+ , the MLCT band at 577 nm (FePT) exhibits a red shift which can be reconfigured to the original spectrum by adding H_2O or Et_3N . Consequently, taking the absorbance at 577 nm as the output (Out1), a combinatorial logic gate can be configured (Figure 10). In addition, due to the slow oxidation of the Os^{2+} center in the triad layer, reaction time is of importance as well. So, considering it as an additional input and taken the changes in the MLCT band at 501 nm ($A_{501\text{ nm}}$) as the output (Out2), another four-input-based logic gate, representing a combination of AND-NOR-AND gates, can be designed (Figure 11). Importantly, the optical readout at $A_{501\text{ nm}}$ can be "RESET" to $A_{508\text{ nm}}$ using In3, while it can be further "SET" using In1. Thus, the triad layer showing the reversible-switching behavior ("SET"/"RESET") can be used to create a feedback loop validating a "Write-Read-Erase-Read" cycle (Figure 11).

Hetero-Dinuclear Terpyridyl Complexes as Ternary Memory Modules

A monolayer comprising Ru^{2+} - and Os^{2+} -based heterodinuclear terpyridyl complexes separated by an organic linker was fabricated on ITO-coated glass, and its optical properties were tuned by applying external bias, viz. +0.6, +1.1, and +1.6 V vs Ag/AgCl (Scheme 6).⁴⁰

Figure 10. Top panel: a combinatorial logic gate comprising NO^+ , H_2O , and Et_3N as input strings, viz. In1, In2, and In3, respectively, while the changes in absorbance at 577 nm are considered as the output (Out1). Bottom panel: truth table for the heterotriad layer (OsPT/Cu/RuPT/Cu/FePT)-based logic gate. Adapted with permission from ref 23. Copyright 2015 American Chemical Society.

The oxidation potentials of the metal centers are separated by 400 mV (Figure 12a), which allows the tuning of the optical properties of the film under selective bias. For a bias within the + (0.6–1.1) V range, Os^{2+} oxidation occurred, with concomitant hypochromic shift of the most-intense $^1\text{MLCT}$ band at $\lambda_{\text{max}} = 503\text{ nm}$ and disappearance of the weaker $^3\text{MLCT}$ band at $\lambda_{\text{max}} = 687\text{ nm}$ (Figure 12b). For a higher bias, within the + (1.0–1.6 V) range, the Ru center was oxidized, with concomitant reduction in absorption at 503 nm. Thus, this molecular film can generate three bias-controlled oxidation states (I, II, and III) of the metal centers, accompanied by changes in the optical spectra (Figure 12b). Chronocoulometry experiments revealed a fast response time for the bit storage/release, viz., 0.49 s/0.38 s for $\text{Os}^{2+/3+}$ and 0.59 s/0.26 s for Os^{3+} and $\text{Ru}^{2+/3+}$ (Figure 12c,d). Moreover, direct oxidation of both metal centers could also be performed in a single-step fashion, applying a high bias (0.6–1.6 V, $\text{Os}^{2+/3+}$ and $\text{Ru}^{2+/3+}$) in 0.66 s (Figure 12e). The

Figure 11. Top panel: combinational logic circuits constructed using NO^+ , reaction time, H_2O , and Et_3N as In1, In2, In3, and In4, respectively, while the absorbance at 501 nm is considered as the output (Out2); the Out2 = 1 only at In1 = In2 = 1 and In3 = In4 = 0; the Out2 = 0 at all other combinations of the inputs. Bottom panel: feedback loop representing a “Write–Read–Erase–Read” cycle upon the chemical input applied to the triad assembly. Adapted with permission from ref 23. Copyright 2015 American Chemical Society.

Scheme 6. Schematic of the Heterometallic Monolayer Prepared on an ITO-coated glass

◆ Showing reconfigurable optoelectronic behavior under the influence of controlled bias (+1.1 and +1.6 V for oxidation and +1.0 and +0.6 V for reduction). (a) the (0,0), (b) (1,0), and (c) (1,1) states correspond to non-oxidized, one-metal-center-oxidized, and both-metal-centers-oxidized cases, respectively.

bias-controlled absorbance states I (at +0.6 V), II (at +1.1 V), and III (+1.6 V) can be associated with the “00”, “10”, and “11” memory states (considering the reduced and oxidized states as equivalent to “0” and “1”, respectively) and serve as basis for prototype ternary information-storage device.

CONCLUDING REMARKS

Controlled assembly of metal–terpyridyl complexes on solid supports enables efficient and broad employment of their optical, chemical, and electrochemical properties as compared to the analogous solution-based systems. In this context, we present here our recent results on the design and fabrication of functional monolayers, dyads, triads, and oligomer films,

Figure 12. (a) CV of the heterometallic monolayer (Scheme 6) at 1.0 V s^{-1} (vs Ag/AgCl); (b) UV–vis absorbance spectra of this monolayer corresponding to its electrochemical switching at potentials of 0.6 V (I), 1.1 V (II), and 1.6 V (III); chronocoulometry curves for 0.6–1.1 V (c), 1.0–1.6 V (d), and 0.6–1.6 V (e). Reproduced with permission from ref 40. Copyright 2014 Royal Society of Chemistry.

composed of the MPT ($\text{M} = \text{Fe}^{2+}$, Ru^{2+} , Os^{2+}) units, on transparent and conductive oxide substrates. The MPT units in these layers are linked via different metal ions or organic struts. The spectro-electrochemical characteristics of multi-MPT assemblies exhibited a superposition of the respective characteristics of the individual metallo-organic complexes providing a significant enlargement of the optical window and showing a variety of well-separated redox peaks. On this basis and also on the basis of the rational design of the individual molecular building blocks, linked to each other chemically and electronically by suitable linkers, a variety of functional, MPT-based films could be designed, targeting specific applications as ion/molecular sensors, molecular catalysts, molecular logic gates, and ternary memory modules.

The metal–terpyridyl-based assemblies on transparent and conductive oxide substrates, as discussed in this Account, are only representative examples of the broad possibilities provided by these systems as also reflected in the reports of other groups.^{41–43} Such and analogous assemblies will certainly become an important part of next-generation molecular sensors and optoelectronic systems, relying on flexible design and widely adjustable properties. The ability of terpyridyl to coordinate different transition-metal ions, with the respective changes in the optical and electronic properties, provides a versatile toolbox for material engineering, paving the way for new technologies if a step from model systems to commercial products can be made. Beyond the examples given in the present Account, possible applications include molecular wires with low attenuation factors ($\beta = 0.028\text{--}0.001 \text{ Å}^{-1}$),^{44–47} electrochemical rectification,¹⁸ three-dimensional integrated circuits,³ fabrication of multifunctional electrochromic elements for color displays, electronic paper, computing,⁴⁸ and many others.

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