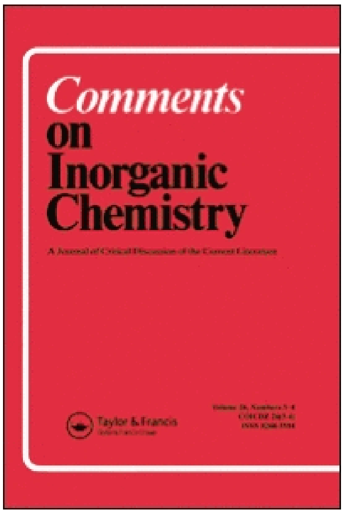

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Hong, Bo(1999) 'Photoresponsive and Redox-Active Supramolecular Systems with Rigid Sp Carbon Chain Spacers', Comments on Inorganic Chemistry, 20: 4, 177 — 207

To link to this Article: DOI: 10.1080/02603599908021443

URL: http://dx.doi.org/10.1080/02603599908021443

Photoresponsive and Redox-Active Supramolecular Systems with Rigid Sp Carbon Chain Spacers

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The construction and investigation of photoresponsive and redox-active supramolecular systems with acetylenyl (polyyne) and cumulenic sp hybridized carbon chains (C_n) are reported here. Novel types of one-dimensional rigid molecular rods and macrocyclic molecular squares with controllable and yet fixed chain lengths or cavity sizes are explored. Such systems will have the desired features such as synthetic accessibility, coordination versatility, rigidity, directionality, photostability, electronic conductivity, controllable distances between donors and acceptors, and controllable cavity sizes in macrocyclic molecular squares. These features are extremely important to the future applications of these new rigid supramolecular systems in molecular photonic and electronic devices, light-energy conversion, molecular recognition, and host-guest chemistry.

In addition to the exploration of synthetic features, the solution state redox characteristics and molecular photophysics of the metal-containing supramolecular systems with sp carbon chains are also under investigation. This includes the modulation of electronic communication between multiple redox centers spanned by rigid spacers of various chain lengths and the study of long-range, directional photoinduced energy/electron transfer across such spacers. In addition, covalent surface confinement of systems containing sp carbon chains is also investigated here. Specifically, UV/vis and X-ray photoelectron spectroscopy have been used as spectroscopic tools to monitor the growth of mono- and multilayer thin films.

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Comments Inorg. Chem.
1999, Vol. 20, No. 4-6, pp. 177-207
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Science Publishers imprint.
Printed in Malaysia

Keywords: *Rigid supramolecules, rigid-rod molecules, macrocyclic molecular squares, cumulenic and acetylenyl (polyyne) sp carbon chains, phosphines, metal complexes, electron/energy transfer, electronic communication, steady-state and time-resolved emission, transient absorption spectroscopy, thin films, covalent surface modification, X-ray photoelectron spectroscopy*

1. INTRODUCTION

One of the current interest in the design of supramolecular systems for applications in functional nanoscale photonic and electronic devices is the construction of suitable molecules that have spatially separated, photo- and/or redox-active subunits.[1–2] To ensure the directionality and also construct multicomponent molecular systems with well-defined structures, rigid spacers are employed to afford restricted conformational mobility and controllable distance between structural subunits.[3–17]

In this work we will incorporate rigid sp carbon chain spacers into the research of novel types of photoresponsive and redox-active molecular rods and macrocyclic molecular squares, Figure 1. Relevant literature studies and significance of such research are discussed in the following sections.

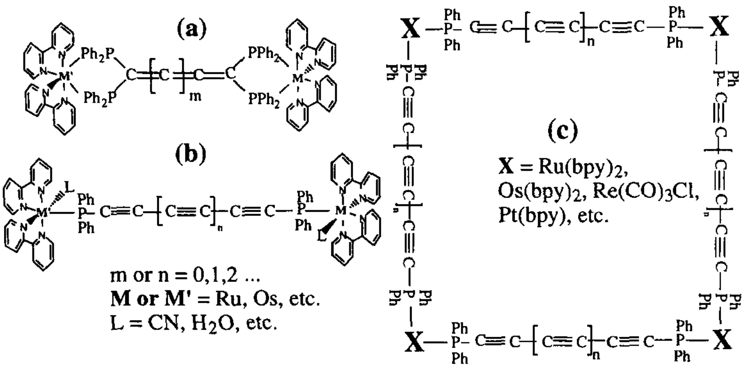
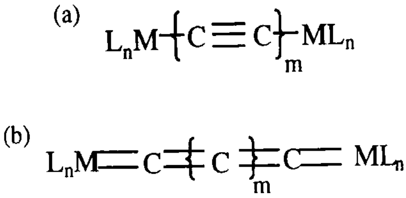


FIGURE 1 Prototypical structures of rigid supramolecular systems with cumulenic and acetylenyl (polyyne) spacers

1.1. Background

In recent years, studies on supramolecular systems with unsaturated sp carbon chains have focused on the one dimensional molecular wires.[3–

[14] Numerous laboratories have investigated the synthetic approaches, structural features, and redox interactions across the sp carbon chains, especially systems with alkyne (acetylenyl or polyyne) spacers.[3–5,10–14] One major type of complexes involves the direct coupling of metals (typically, Mn, Re, Rh, Ir, Ni, Pd, Pt, Fe) with the terminal carbon atoms of acetylenyl (Figure 2a) or cumulenic chains (Figure 2b).[3,4,12,13–16] No photophysical properties of such systems are reported, to our best knowledge. Recently Therien and coworkers[5] have constructed light-harvesting systems using metalloporphyrins bridged by short acetylenyl (C_2 or C_4) chains. Ziessel *et al.*[10] have reported Ru^{II}/Os^{II} terpyridyl complexes with C_2 and C_4 alkyne bridges. In both systems metal centers are no longer directly linked to the terminal carbons, but rather through a "linkage component", such as a porphyrin or a terpyridine unit. Efficient electronic and excitonic coupling across these short C_2 and C_4 chains are reported.[5,10] The rate constants of intramolecular energy transfer are as high as $7.1 \times 10^{10}\ s^{-1}$.[10b]



$$L_nM\left[C\equiv C\right]_m ML_n$$

$$L_nM{=}C{=}\left[C\right]_m{=}C{=}ML_n$$

FIGURE 2 Prototypical structures of the known metal complexes bridged by acetylenyl (a) and cumulenic (b) chains

Despite the applications of short acetylenyl sp carbon chain spacers in molecular wires, these spacers have been largely unexplored in the construction of metal-containing macrocyclic molecular squares (also called inorganic cyclophanes). Currently the majority of known rigid, square box-like supramolecules consist of *cis*-metal centers connected by aromatic bridges and pyridine-type of spacers.[17–20] They have emerged as promising new systems within the realm of self-assembly metal-containing macrocycles, host-guest, inclusion, and molecular recognition chemistry.[17–20] Significant efforts have been made towards the systems derived from Pt(II) or Pd(II) species with N-containing ligands, reported by Stang,[18] Fujita,[19] and others.[20a–b] Recently Hupp, et al.[17]

have studied the luminescent metal-ligand components within a square assembly containing pyridine-type of spacers. Specifically, systems with neutral Re_4 or charged Re_2M_2 (M = Pd, Pt) are reported. Despite the above interesting studies, macrocyclic systems with other photo- and redox-active metal centers and spacers other than the aromatic and pyridine-type of bridges are not much explored.

1.2. Scope and significance

The study of photoresponsive and redox-active supramolecular systems with C_n chains will encompass the basic issues of electronic communication and molecular photophysics of supramolecular systems with rigid π-bonded sp carbon chains. This will include the influence of distances or spacer chain lengths on the efficiencies and the rate constants of electron/energy transfer, the excited state decay paths and decay kinetics, and the energetics of directional electron/energy transfer. The use of cumulenic and acetylenyl sp carbon chains will introduce new structural features and significant advantages, including synthetic accessibility, coordination versatility, rigidity, directionality, photostability, electronic conductivity, well defined structures, controllable distances between donors and acceptors, and controllable cavity sizes in macrocyclic molecular squares. In addition, cumulenic and acetylenyl sp carbon chains are excellent spacers (or conduits) that will promote electron/energy transfer without direct participation in the process. Initial solution state UV/vis study by Walton et al.[4b] found no significant absorption beyond 370 nm for oligomeric polyynes $Et_3Si(C{\equiv}C)_nSiEt_3$, even with chain lengths as long as C_{20}! No significant overlap in absorption of the spacers and the metal-based chromophores are expected (excitation wavelengths of chromophores are usually beyond 450 nm in our systems). Another excellent and desired property of the compounds with sp carbon chains is their high solubility in various organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH, MeCN, or THF.[3,4b]

Although short alkyne chains (C_2 and C_4) have been incorporated in photoresponsive supramolecules, systematic studies and kinetic data of systems with cumulenic chains and longer acetylenyl chains are scarce. There is also a lack of knowledge regarding the similarity and differences between the photoactive supramolecular systems with cumulenic spacers vs. the systems with acetylenyl ones. Furthermore, interesting structural differences exist between acetylenyl and cumulenic spacers. While acetylenyl chains are conjugated, each odd carbon in the cumulenic chains will place the terminal groups at 90° angle relative to each other. Such structural changes may result in interesting modification in the photophysical and electrochemical properties of these systems. These new supramolecules will also afford us an excellent opportunity to compare the systems of one-dimensional C_n chains with others containing polyphenyls,[21,22] rigid alkanes,[23–24] steroid,[25] and alkenes[26] in mediating photoinduced electron/energy transfer.

Incorporation of photo- and redox-active centers into macrocyclic molecular squares is attractive in the eventual molecular sensing technology. Such application suggests alternative ways to the detection of guest inclusion based on photoluminescence characteristics[17] or changes in NMR chemical shift values.[19] The spacers used in the previous studies are predominantly aromatic and pyridine-type bridges.[17,18] In our systems, new types of spacers with acetylenyl sp carbon chains will be incorporated into macrocyclic molecular squares. Furthermore, the existence of four photo- and redox-active metal centers within rigid square framework affords excellent opportunities to study the electronic and excitonic interaction among the active metal centers within well-defined square structures. One additional advantage is that we can tune the cavity sizes using acetylenyl spacers with different chain lengths. As a result, a novel series of rigid molecular squares with controllable cavity sizes can be constructed for the applications in molecular recognition, inclusion, and host-guest chemistry.

We will also introduce the metal-phosphine photosensitizers as light absorbing and emitting chromophores into the rigid rods and macrocyclic molecular squares. Phosphines are chosen as the linkage components since they can serve as excellent complexing ligands toward a large number of transition metal centers such as Ru, Os, Rh, Ir, Pt, Pd, Re, etc.[27,28] Phosphines are also much less explored in the photo- and redox-active supramolecules when compared with N-containing ligands such as polypyridyl, nitrile, or amine ligands.[2,21,22] In addition, previous work by Meyer[29], Brewer,[30] and Fox[31] have revealed that replacing one of the polypyridyl ligands with phosphines (i.e., PPh_3, $Ph_2PCH_2CH_2PPh_2$, etc.) in Os^{II}-polypyridyl complexes can enhance the excited state lifetimes and quantum yields of ^{3}MLCT states. Long-lived excited state and high luminescence quantum yields are preferred in the studies of photoinduced electron/energy transfer, charge separation, and the construction of supramolecular photochemical systems for light-energy conversion. This is simply due to the fact that short-lived excited states will decay to ground states before the desired electron/energy transfer processes are accomplished.

In addition to the exploration of synthetic aspects of rigid spacers with sp carbon chains and their supramolecular systems, we are also interested in the assembly of these systems, especially the metal-containing ones, on surface. Well-defined monolayers and multilayers containing chromophores and redox-active centers are important due to their diverse applications in photocatalysis, light-harvesting, nonlinear optical materials, and sensor technology.[32–35] In section 6, the preparation of monolayers and multilayers containing covalently confined metal-based chromophores with sp carbon chains will be described, followed by the characterization using, e.g., electronic absorption and X-ray photoelectron spectroscopy.

Overall, through the use of C_n spacers two important types of supramolecular systems, molecular rods and molecular squares, are uniquely combined together in the study of supramolecular photophysics and electronic communication. Synthetically these two systems are closely related to each other. By changing the metal-to-spacer ratios we can synthesize either molecular rods (e.g., 2:1 metal:spacer ratio) or molecular squares (e.g., 1:1 metal:spacer ratio) with acetylenyl spacers. They both afford excellent opportunities to study photophysical and electrochemical properties of supramolecular systems with rigid C_n chains.

2. SYNTHESIS OF RIGID-ROD SPACERS

In our study of supramolecular systems with rigid C_n chains, the preparation of spacers is a key step. In this section, the synthetic approaches to spacers and their corresponding precursors with various chain lengths will be addressed.

2.1. Spacers with cumulenic bridges

Ditopic ligand **C_2P_2e** was prepared as shown in Figure 3a from treatment of PPh_3 with lithium in THF followed by *in situ* reaction with

$H_2C{=}CCl_2$.[36–37] This ligand is primarily used in the preparation of monometallic precursors or model compounds in photophysical studies.

To prepare spacers with odd or even number of carbon atoms, different synthetic approaches must be taken.[36,37] Figure 3b gives the representative approaches to spacer $\mathbf{C_3P_4}$ with allene bridge, starting from monophosphine precursor $CH_3C{\equiv}CPPh_2$ by treatment with Bu^nLi followed by *in situ* reaction with $ClPPh_2$. Spacer $\mathbf{C_4P_4}$ with cumulene bridge, on the other hand, was prepared from diphosphine precursor $Ph_2PC{\equiv}CPPh_2$ ($\mathbf{C_2P_2a}$) by treatment with $KPPh_2$ and the subsequent *in situ* reaction with $ClPPh_2$. Currently we are exploring the synthetic approaches to the tetratopic spacers with longer C_n chains using similar approaches.

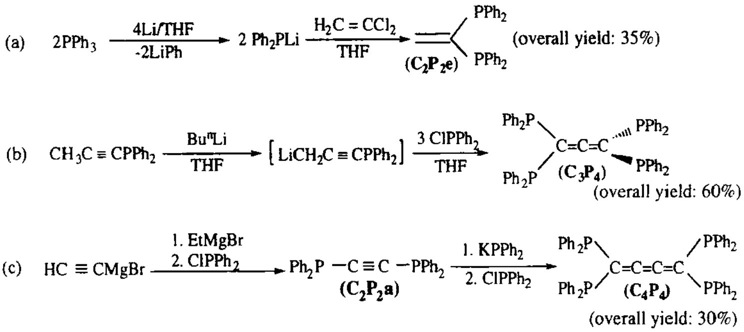


FIGURE 3 Preparation of spacers with cumulenic chains

2.2. Spacers with acetylenyl (polyyne) bridges

To prepare ditopic spacers with acetylenyl bridges of various chain lengths, the molecular precursors $Me_3Si(C{\equiv}C)_{n/2}SiMe_3$ ($\mathbf{C_nSi_2}$, n = 2, 4, 6....) are treated with two equivalents of MeLi, followed by an *in situ* reaction of the lithiated intermediate with two equivalents of Ph_2PCl to give the desired $\mathbf{C_nP_2}$ compounds, Figure 4a. In order to prepare precursors with longer carbon chain lengths such as $\mathbf{C_8Si_2}$, the Cu^I-catalyzed coupling[3] is conducted, using, e.g., two equivalents of $Me_3Si\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H$ ($\mathbf{C_4SiH}$). To prepare precursors such as $\mathbf{C_6Si_2}$, where starting materials with odd number carbon chain are not available for coupling reaction, cross coupling of a 50:50 mixture of $\mathbf{C_4SiH}$ and

C_2SiH is used. All new spacers and their precursors are fully characterized by ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR, as well as mass spectral analysis.

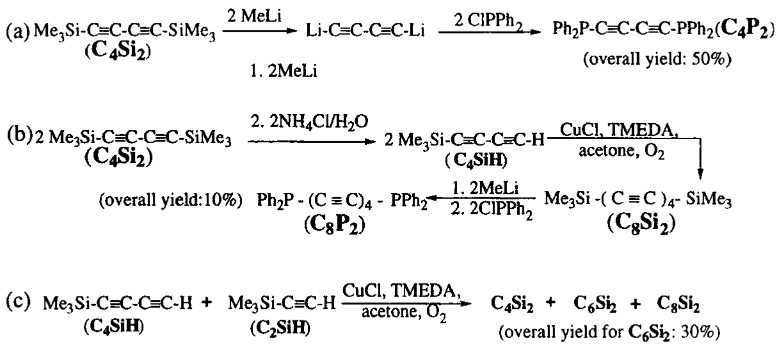


FIGURE 4 Preparation of spacers with acetylenyl chains

3. MOLECULAR RODS AND SQUARES SYNTHESIS

3.1. Synthetic features

Since spacers with phosphine linkage groups have high reactivity, synthetic versatility, and chemical stability, they can be used as primary molecular building blocks for the construction of supramolecular systems. Because of the specific spatial arrangements of spacers and the desired structures (Figure 1), both spacers with cumulenic and acetylenyl (polyyne) bridges are suitable candidates for the construction of one-dimensional molecular wires (Figure 1a-b), while only acetylenyl ones will be studied for the assembly of macrocyclic molecular squares (Figure 1c).

Precursors

The following compounds are suitable molecular precursors for monometallic or multicenter systems: *cis*-$M(bpy)_2Cl_2$ (M = Ru, Os), $M(bpy)_2(CO_3)$ (M = Ru, Os), *cis*-$M(P)_2Cl_2$(M = Ni, Pd, Pt; P = phosphine), *cis*-$M(MeCN)_2Cl_2$ (M = Pd, Pt), M(tpy)(bpy)L (L = Cl, H_2O, or acetone, M = Ru, Os), or $Re(CO)_5Cl$.[21,22,31,36,38] They can be used to directly react with the spacers to give monometallic, homobimetallic, or tetrametallic systems.

To prepare heterometallic systems with the combination of donor/acceptor for electron/energy transfer, a stepwise approach has to be taken. This includes the initial preparation of the suitable monomeric complexes from the above precursors and spacers $\mathbf{C_nP_m}$(m = 2, n = 2, 4, 6,...; m = 4, n = 2, 3, 4, ...), followed by further reaction of purified monomeric species with the corresponding precursors of a second type of metal center.

Metal-to-spacer ratio

Such ratio plays an important role in determining the major products of reactions between spacers and the suitable metal-based precursors. The tetratopic spacers with cumulene bridges can serve as bischelating (Figure 5a), monodentate (Figure 5b), or tetradentate ligand (Figure 5c) in the formation of species with one or two metal centers. To ensure the formation of monometallic systems, an excess amount of spacers (usually 2.2–3:1 spacer-to-metal ratios) must be used. On the other hand, to ensure the formation of homobimetallic species, a low spacer-to-metal (typically 1:2.2) must be used. An extended reaction time[36,38] is required in all preparations in order to obtain the desired complexes with bis- or tetrachelating spacers. This is partly due to the fact that a four-member chelate ring is formed. Purification of desired compounds can be accomplished by column chromatographic separation using basic alumina and acetonitrile or acetonitrile/toluene eluents.

Similar synthetic strategies can be used to obtain rigid rod-like structures with polyyne spacers. Typically, excess spacers (high spacer-to-metal ratios such as 2.2–5:1) is used for the preparation of monometallic species, while low spacer-to-metal ratios (such as 1:2.2–3) is used to ensure the formation of multimetallic systems.

In order to obtain the macrocyclic molecular squares, a typical spacer-to-metal ratio of 1:1 is used to afford the desired products, Figure 6. Although both molecular squares and linear polymers are possible products using this ratio, it is found that high dilution of reactants can enhance molecular cycle formation relative to polymer formation.[17c]

3.2. Structural identification using FAB/MS and MALDI-TOF/MS analyses

The determination of structures and relative molecular masses of metal-containing supramolecular systems are major challenges in this

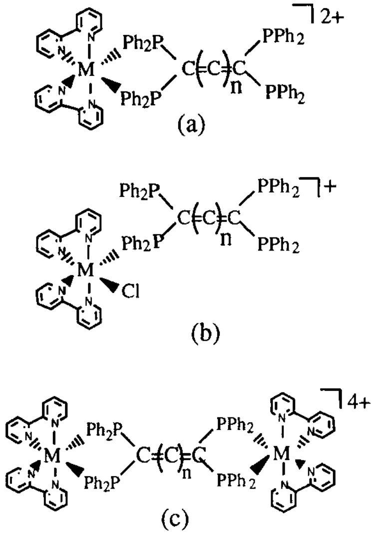


FIGURE 5 Possible coordination modes for tetrotopic spacers with cumulenic bridges

field, especially in high molecular weight rigid-rod and macrocyclic molecular systems. Commonly employed methods, such as X-ray structural determination and gel permeation chromatography (GPC), are limited by conditions such as availability of X-ray quality single crystals and the feasibility of GPC analysis of metal-containing supramolecular systems.[39] We have successfully employed fast atom bombardment (FAB/MS) and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) to accurately identify new spacers and their mono- and multicomponent metal complexes, in addition to ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ NMR study and elemental analysis.

Several interesting features exist in our FAB/MS study. First, FAB/MS is a relatively soft ionization technique for our metal complexes. Many of the observed fragment ions only involve the sequential loss of counterions (PF_6) and PPh_2 units. In addition, the spectra contain numerous informative peaks with the isotope distributions identical to the computer simulated ones, allowing the straightforward identification of new spacers and supramolecular complexes.[36,38] Figure 7a shows a

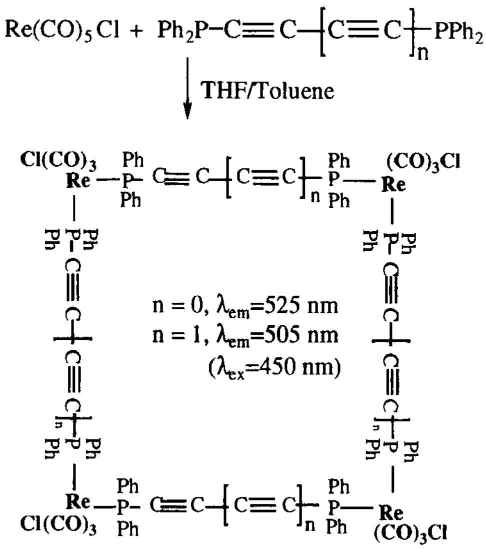


FIGURE 6 Preparation of macrocyclic molecular squares with Re(I) centers

representative pattern of fragmentation in FAB/MS analysis of $[Os(bpy)_2(C_3P_4)](PF_6)_2$, and Figure 8 gives the representative comparison between the simulated and observed isotope patterns of the tetrametallic molecular fragment $(M - Cl)^+$ $(M = [Re(CO)_3Cl(C_4P_2)]_4)$.

It is also found that although all metal complexes with polyphosphines are very stable in air (no additional peaks corresponding to the oxidized PPh_2 units are observed in the ^{31}P NMR spectra of these complexes), oxidation of PPh_2 unit to $OPPh_2$ in spacers and their metal complexes were observed during the FAB/MS analysis, Figure 7. In a control experiment using both EI/MS and FAB/MS analysis of C_3P_4, Figure 7b, FAB/MS gives a complicated spectrum with peaks corresponding to the spacer itself (M^+, *m/z* 777) and the oxidized ones (*m/z*: M^++O 793; M^++2O 809; M^++3O 825), while EI/MS gives a clean spectrum without any peaks corresponding to $OPPh_2$ units for the same sample (inset in Figure 7b).

The matrix-assisted laser-desorption ionization time-of-flight mass spectral analyses (MALDI-TOF/MS) of complexes with allene and cumulene chains are also carried out. Figure 9 displays the mass spec-

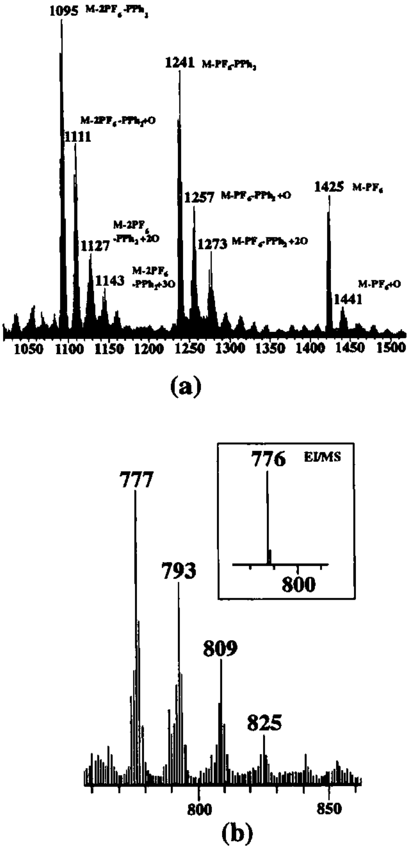


FIGURE 7 FAB/MS analysis of $[Os(bpy)_2(C_3P_4)](PF_6)_2$ (a) and comparison of EI/MS (inset) and FAB/MS analysis of C_3P_4 (b)

trum of **RuC_4Os** with a representative fragmentation pattern. Typically, the fragmentation process involves the consecutive loss of PF_6, PPh_2, and F, as well as addition of O atom.

4. ELECTRONIC COMMUNICATION AND REDOX ENERGETICS

Spacers with cumulenic or acetylenyl chains have their unique structural features that render them interesting systems in the study of redox inter-

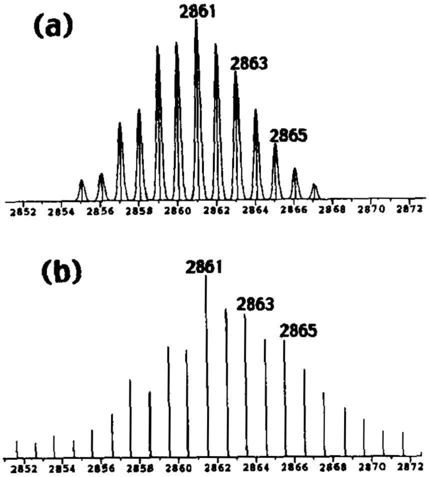


FIGURE 8 Computer simultaed (a) and observed isotope patterns for the molecular fragment $\{[Re(CO)_3Cl(P_2C_4)]_4\text{- }Cl\}^+$

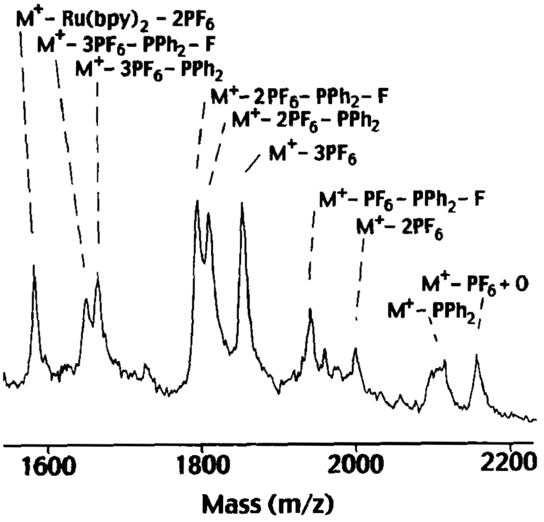


FIGURE 9 Fragmentation pattern in MALDI-TOF/MS of $[(bpy)Ru(\mathbf{C_4P_4})Os(bpy)_2](PF_6)_4$(**$RuC_4Os$**)

action across rigid unsaturated bridges. While acetylenyl spacers are conjugated, the cumulenic chains with odd number of carbon atoms will place the terminal groups at 90° angle relative to each other. In this section the electrochemical properties of mono- and homobimetallic systems with C_n (n = 2, 3, 4) chain lengths are compared (Table I & II), and studies on systems with longer chain lengths are undergoing in our laboratory.

4.1. Modulation of electronic communication using spacers with cumulenic chains

The metal-based redox potentials of mono- and bimetallic systems with C_2, C_3, and C_4 cumulenic chains are compared in Table I. Interesting features are observed. First, all monometallic systems exhibit single reversible one-electron process with the $i_p{}^a/i_p{}^c$ value being approximately unity, corresponding to $M^{II/III}$ redox couple (M = Ru or Os). Second, the C_n-bridged spacers have profound influence on the metal-based oxidations. As the carbon chain length increases, the $M^{II/III}$ redox potential continuously shifts significantly to less positive values, Table I. In other words, the oxidation of M(II) center (M = Ru, Os) becomes more thermodynamically favored with longer carbon chains in rigid spacers.

In addition to above characteristics, the homobimetallic complexes **MC_3M** (M = Ru or Os) feature two overlapping one-electron processes, while the corresponding **MC_4M** (M = Ru or Os) complexes have two consecutive one-electron processes, Figure 10. This is ascribed to the difference in the electronic communication between two terminal subunits resulting from the change of C_3 to C_4.

For the binuclear complexes that can undergo multi-step charge-transfer, Equation (1), the equilibrium constant (K_c) for the comproportionation reaction is defined as shown in Equation (2), with $\Delta E° = E_1° - E_2°$ in mV and at 298 K.[40]

$$M^{n+}M^{n+} \underset{e^-}{\overset{E_1^0}{\rightleftharpoons}} M^{(n-1)+}M^{n+} \underset{e^-}{\overset{E_2^0}{\rightleftharpoons}} M^{(n-1)+}M^{(n-1)+} \qquad (1)$$

$$K_c = \frac{[M^{(n-1)+}M^{n+}]^2}{[M^{n+}M^{n+}][M^{(n-1)+}M^{(n-1)+}]} = \exp[(E_1^0 - E_2^0)/25.69] \qquad (2)$$

TABLE I Summary of electrochemical and photophysical data for selected monomeric and homobimetallic systems with cumulenic C_n (n = 2, 3, 4) spacers. [a]

Complex	$E_{1/2}$ ($M^{II/III}$), ΔE_p (*vs. SCE*)	λ_{EM}, *nm*	τ_{EM} (*ns*), *Ru-centered* (±*15%*)	τ_{EM} (*ns*), *Os- centered* (±*15%*)
$(bpy)_2Ru(C_2P_2e)(PF_6)_2$ ($\mathbf{RuC_2}$)	+1.70 (1e$^-$, 80)	530	25	
$(bpy)_2Ru(C_3P_4)(PF_6)_2$ ($\mathbf{RuC_3}$)	+1.55 (1e$^-$, 70)	535	40	
$(bpy)_2Ru(C_4P_4)(PF_6)_2$ ($\mathbf{RuC_4}$)	+1.07 (1e$^-$, 82)	540	15	
$(bpy)_2Os(C_2P_2e)(PF_6)_2$ ($\mathbf{OsC_2}$)	+1.35 (1e$^-$, 76)	600		190
$(bpy)_2Os(C_3P_4)(PF_6)_2$ ($\mathbf{OsC_3}$)	+1.12 (1e$^-$, 74)	570		350
$(bpy)_2Os(C_4P_4)(PF_6)_2$ ($\mathbf{OsC_4}$)	+0.80 (1e$^-$, 62)	590		410
$[(bpy)_2Ru]_2(C_3P_4)(PF_6)_4$ ($\mathbf{RuC_3Ru}$)	+1.07 (2e$^-$, 96)	560	45	
$[(bpy)_2Ru]_2(C_4P_4)(PF_6)_4$ ($\mathbf{RuC_4Ru}$)	+1.01 (1e$^-$, 69), +1.43 (1e$^-$, 63)	595	820	
$[(bpy)_2Os]_2(C_3P_4))(PF_6)_4$($\mathbf{OsC_3Os}$)	+0.77 (2e$^-$, 100)	575		520
$[(bpy)_2Os]_2(C_4P_4)(PF_6)_4$ ($\mathbf{OsC_4Os}$)	+0.72 (1e$^-$, 78) +1.35 (1e$^-$, 76)	660		480
$[(bpy)_2Ru(C_3P_4)Os(bpy)_2])(PF_6)_4$ ($\mathbf{RuC_3Os}$)	+0.98 (1e$^-$, 82), +1.63 (1e$^-$, 73)	590	0.33	410
$[(bpy)_2Ru(C_4P_4)Os(bpy)_2](PF_6)_4$ ($\mathbf{RuC_4Os}$)	+0.74 (1e$^-$, 83), +1.32 (1e$^-$, 67)	660	~ 0.01	160

[a] In deoxygenated acetonitrile at 22 °C.

TABLE II Summary of electrochemical and photophysical data for selected monomeric and homobimetallic systems with acetylenyl C_n (n = 2, 4) spacers. [a]

Complex	$E_{1/2}$ $(M^{II/III})$, ΔE_p *(vs. SCE)*	λ_{EM}, *nm*	τ_{EM} *(ns), Ru-centered (±15%)*	τ_{EM} *(ns), Os- or Recentered (±15%)*
$(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{C_2P_2a})\mathrm{Cl}(\mathrm{PF_6})$ (**$\mathbf{ClRuC_2}$**)	+1.020 (1e$^-$, 70)	595	715	
$(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{C_4P_2})\mathrm{Cl}(\mathrm{PF_6})$ (**$\mathbf{ClRuC_4}$**)	+1.044 (1e$^-$, 90)	510	40	
$(\mathrm{bpy})_2\mathrm{Os}(\mathrm{C_2P_2a})\mathrm{Cl}(\mathrm{PF_6})$ (**$\mathbf{ClOsC_2}$**)	+0.645 (1e$^-$, 59)	610		515
$(\mathrm{bpy})_2\mathrm{Os}(\mathrm{C_4P_2})\mathrm{Cl}(\mathrm{PF_6})$ (**$\mathbf{ClOsC_4}$**)	+0.666 (1e$^-$, 67)	520		65
$[(\mathrm{bpy})_2\mathrm{RuCl}]_2(\mathrm{C_2P_2a})(\mathrm{PF_6})_2$ (**$\mathbf{ClRuC_2RuCl}$**)	+1.105 (1e^{-*}) +1.037 (1e^{-*})	595	370	
$[(\mathrm{bpy})_2\mathrm{RuCl}]_2(\mathrm{C_4P_2})(\mathrm{PF_6})_2$ (**$\mathbf{ClRuC_4RuCl}$**)	+1.058 (2e$^-$, 100)	510	40	
$[(\mathrm{bpy})_2\mathrm{OsCl}]_2(\mathrm{C_2P_2a})(\mathrm{PF_6})_2$ (**$\mathbf{ClOsC_2OsCl}$**)	+0.709 (1e^{-*}) +0.635 (1e^{-*})	555		525
$[(\mathrm{bpy})_2\mathrm{OsCl}]_2(\mathrm{C_4P_2})(\mathrm{PF_6})_2$ (**$\mathbf{ClOsC_4OsCl}$**)	+0.705 (2e$^-$, 99)	530		90
$[(\mathrm{bpy})_2\mathrm{RuCl}(\mathrm{C_2P_2a})\mathrm{ClOs}(\mathrm{bpy})_2](\mathrm{PF_6})_2$ (**$\mathbf{ClRuC_2OsCl}$**)	+1.101 (1e$^-$, 63) +0.681 (1e$^-$, 65)	595	<10 **	620
$[(\mathrm{bpy})_2\mathrm{RuCl}(\mathrm{C_4P_2})\mathrm{ClOs}(\mathrm{bpy})_2](\mathrm{PF_6})_2$ (**$\mathbf{ClRuC_4OsCl}$**)	+1.057 (1e$^-$, 62) +0.671 (1e$^-$, 65)	530	<10 **	215
$[\mathrm{Re(CO)_3Cl(C_2P_2a)}]_4$	-	525		< 10 **
$[\mathrm{Re(CO)_3Cl(C_4P_2)}]_4$	-	505		< 10 **

[a] In deoxygenated acetonitrile at 22 °C.

[*] Data measured using square wave voltammetry.

[**] Lifetimes were found to be shorter than 10 ns in our current nanosecond laser system. Further measurements will be made to obtain the accurate lifetimes.

Stationary cyclic voltammetry can be applied to determine the ΔE° value by estimation from $\Delta E_{1/2}$.[40a] From $\Delta E_{1/2}$ a quantitative measure of the energetics for the comproportionation reactions can be achieved and K_c values may range from 4 in the uncoupled Robin and Day Class I systems to 10^{13} in strongly coupled Class III systems.[41] For our homobimetallic complexes **MC_4M** (M = Ru, Os), the calculated K_c values are 1.3×10^7 for M = Ru ($\Delta E_{1/2} = 420$ mV) and 4.5×10^{10} for M = Os ($\Delta E_{1/2} = 630$ mV). Such K_c values are comparable or larger than that reported for species with strong electronic interaction between the two redox centers spanned by rigid spacers such as pyrazine.[40,41] In addition, **OsC_4Os** complex has a much greater K_c value than that of the corresponding **RuC_4Ru** complex. This difference in the electronic coupling in systems with Ru(II) and Os(II) can be ascribed to increasing M-L interaction by virtue of dπ-Lπ* mixing (L represents the spacer). Other representative examples include the interaction between two $Ru(NH_3)_5$ units ($\Delta E_{1/2} = 390$ mV) and $Os(NH_3)_5$ units ($\Delta E_{1/2} = 760$ mV) bridged by pyrazine.[41]

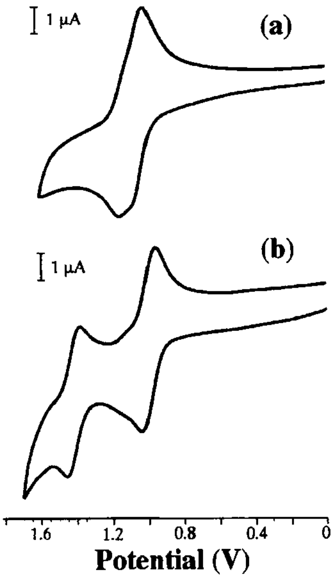


FIGURE 10 Metal-based oxidations in cyclic voltammograms of **RuC_3Ru** (a) and **RuC_4Ru** (b)

When a molecule contains two non-interacting metal centers, it is expected that the current-potential response in stationary cyclic voltammetry to be the same as a single-step charge transfer from a monomeric center.[40,42] The observed metal-based oxidations of **MC_3M**(M = Ru, Os) correspond to two overlapping one-electron processes. Hence, the electronic interaction between two metal centers spanned by **C_3P_4** spacer with allene bridge is rather weak, giving apparently simultaneous one-electron oxidation of two metal centers.

In conclusion, with the fine tune of the number of carbon atoms in the rigid rod-like C_n chains, we can control the electronic interaction (or communication) between the two terminal redox centers. Further investigation will be conducted to study the modulation of redox communication across cumulenic chains with longer lengths.

4.2. Redox interaction across spacers with acetylenyl (polyyne) chains

Table II and Figure 11 give the comparison between the metal-based oxidations in systems with one or two redox centers spanned by ditopic spacers with acetylenyl C_2 or C_4 bridges. Reversible one-electron oxidations are found for all monometallic complexes, however, less change in redox potentials are observed, upon increasing carbon chain length, when compared with systems with cumulenic chains. Only small shifts (*ca.* 0.020 V) toward positive potentials are observed when changed from C_2 to C_4.

The homobimetallic complexes exhibit, as expected, decreasing redox interaction across acetylenyl bridges when the chain length is increased from C_2 to C_4. Two oxidation waves are observed, with peak separation of 74 mV and 68 mV for **$ClOsC_2OsCl$** and **$ClRuC_2RuCl$** using square wave voltammetry, while only one wave is observed for **$ClMC_4MCl$** (M = 2, 4). The comproportionation constant K_c is hence calculated as 14–18 for **$ClMC_2MCl$** (M = Ru, Os) complexes, which corresponds to weakly coupled systems.

5. MOLECULAR PHOTOPHYSICS

We are interested in the study of energetics, the rate constants, and the distance dependence of directional electron/energy transfer across rigid

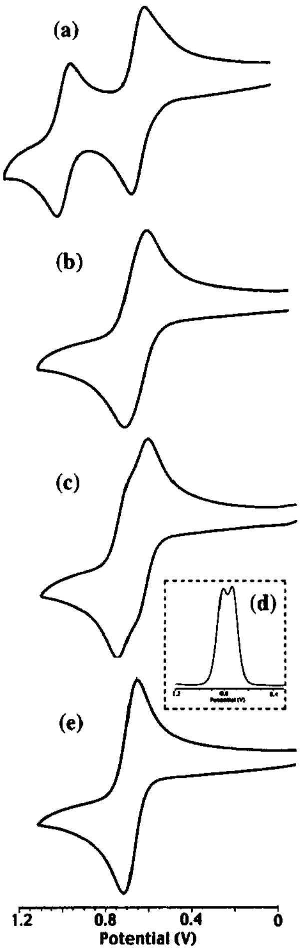


FIGURE 11 Metal-based oxidations in the cyclic voltammograms of **$\mathrm{ClRuC_4OsCl}$** (a), **$\mathrm{ClOsC_4OsCl}$** (b), **$\mathrm{ClOsC_2OsCl}$** (c), **$\mathrm{ClOsC_2}$** (e), and square wave voltammogram of **$\mathrm{ClOsC_2OsCl}$** (d)

sp carbon chains. Electronic absorption, steady-state and transient absorption and emission studies will be used to determine the ground state properties, the excited state decay kinetics, and the existence of any possible transient species.

5.1. Luminescence characteristics

Systems with cumulenic bridges

As summarized in Table I& II, all complexes with cumulenic and acetylenyl bridges emit at wavelengths over 500 nm. For **RuC_n** complexes with ethene, allene, or cumulene bridges, short lived triplet excited states are observed (τ_{EM} = 25, 40, and 15 ns for n = 2, 3, 4, respectively) in comparison with $Ru(bpy)_3(PF_6)_2$ (λ_{EM} = 582 nm, τ = 960 ns[29,30]). Presumably this is due to the mixing between charge transfer band and (higher energy) metal-centered excited states. On the contrast, **OsC_n** exhibits much longer lived ^{3}MLCT excited state (τ = 190, 350, 410 ns for n = 2, 3, 4, respectively) when compared with the corresponding $Os(bpy)_3(PF_6)_2$ (λ_{EM} = 746 nm, τ = 60 ns[31]). This change in Os-based excited states is in consistent with that predicted by the energy gap law[29]: the replacement of one of the σ-donating polypyridyl ligand with phosphine ligands can result in decrease of the nonradiative decay rate due to increase of the energy gap between the emitting MLCT excited state (largely triplet in character) and the singlet ground state. Correspondingly, all emission from monomeric complexes with phosphines shift significantly toward higher energy. Typically such a blue shift is expected when a stronger ligand (such as polyphosphine) is used to replace a relatively weaker ligand (such as bpy).

For homobimetallic complexes **MC_nM,** both Ru and Os complexes have red-shifted emission maxima (Table I) when compared with the corresponding monomeric species **MC_n**, indicative of lower triplet energy in bimetallic complexes. Lowering of the triplet energy may inhibit mixing between the MLCT triplet and higher energy metal- or ligand-centered excited states. Such decoupling of the states will also result in the prolongation of the triplet lifetimes[10a,36] and is largely responsible for the observed longer lifetimes in homobimetallic species.

Systems with acetylenyl bridges

Preliminary studies have been performed on the steady-state emission of rigid-rods and macrocyclic molecular squares with acetylenyl bridges. Specifically, the ^{3}MLCT excited state of Ru(II) and Os(II) systems with $Ph_2PC{\equiv}CPPh_2$ (**C_2P_2a**) spacer exhibit much longer lifetimes than the corresponding systems with $Ph_2PC{\equiv}C\text{-}C{\equiv}CPPh_2$ (**C_4P_2**). Also upon increase of carbon chain length, blue shift of emission maxima is observed (Table II), despite the fact that different metal centers (e.g., Ru(II), Os(II) or Re(I)) are used and different molecular architectures involved. Specifically, a relatively large blue shift, especially in monomeric complexes (*ca.* 90 nm), was observed upon increase of chain length from C_2 to C_4 in Ru(II) and Os(II) complexes. However, relatively small blue shift is observed in homobimetallic Os(II) and mixed metal Ru(II)/Os(II) complexes (*ca.* 10 – 25 nm), as well as in macrocyclic tetrametallic Re(I) complexes (*ca.* 20 nm). Questions remain to be addressed regarding the cause of such shift, and the trend of emission maxima in systems with longer acetylenyl chains.

5.2. Rate of energy/electron transfer

The rate constants for either energy or electron transfer can be experimentally estimated as $k = (1/\tau) - (1/\tau_0)$.[20,31,43,44] Here, τ and τ_0, respectively, refer to the lifetimes of the actual heterometallic complex and the suitable model compounds of the chromophores, such as $\mathbf{MC_n}$ or $\mathbf{MC_nM}$ (M = Ru, Os; n = 3, 4, etc.). All model compounds should have the same oxidation states, inner coordination spheres, and counteranions as the actual chromophores in the heterometallic complexes. The rate constants are hence estimated as *ca.* 3×10^9 s^{-1} for $\mathbf{RuC_3Os}$ and 1×10^{11} s^{-1} for $\mathbf{RuC_4Os}$, using corresponding homobimetallic $\mathbf{RuC_nRu}$ as model compounds. The difference in these rate constants of energy transfer can be ascribed to the aforementioned fact that the electronic communication across a conjugated C_4 bridge is much stronger than across a C_3 bridge. For heterobimetallic systems with acetylenyl C_2 or C_4 chains, the energy transfer rate constants are estimated to be at least 10^8 s^{-1}.

5.3. Transient absorption spectroscopy

As shown in Figure 12, the differential absorption spectra of complexes with cumulenic bridges and Ru(II)/Os(II) centers are characteristic with absorption in the near-UV region (corresponding to the absorbing $\pi \rightarrow \pi^*$ of coordinated bipyridine) and bleaching of m.l.c.t. absorption band in the region of 410 – 550 nm. No other transient species were detected and the excited states decay *via* single exponential kinetics to reform the ground states. Transient absorption studies of other systems are currently under investigation.

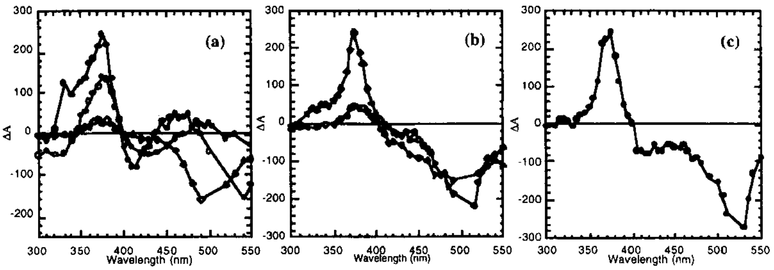


FIGURE 12 Comparison of differential absorption spectra recorded in deoxygenated acetonitrile at 22 °C for the triplet states of (a) $\mathbf{OsC_2}$ (•, excitation at 520 nm), $\mathbf{OsC_3}$ (O, excitation at 520 nm), and $\mathbf{OsC_4}$ (◊, excitation at 520 nm); (b) $\mathbf{OsC_3Os}$ (◊, excitation at 510 nm), $\mathbf{OsC_4Os}$ (♦, excitation at 510 nm); and (c) $\mathbf{RuC_4Ru}$ (excitation 520 nm). All spectra were recorded at 150 ns after laser pulse (pulse width 6 ns)

6. COVALENT SURFACE CONFINEMENT OF SYSTEMS WITH SP CARBON CHAINS

In this section, the preparation of monolayers and multilayers containing covalently confined metal-based chromophores is described, followed by the subsequent characterization using, e.g. electronic absorption and X-ray photoelectron spectroscopy. Specifically, chromophores containing osmium/polypyridine and osmium complexes of C_n bridges are used. Such complexes have been found to be photostable and their solution state absorption, luminescence, and redox properties have been studied. Upon incorporation into the self-assembled organosilane monolayer structures via covalent linkage, surface confined osmium-based chromophore units, in combination with other building block modifications, may allow the expedient assembly of robust monolayer and multilayer structures.

6.1. Chemical modification processes

Figure 13 illustrates our present approach to Os-containing monolayers and multilayers on polycrystalline quartz surfaces. The terminal $OsCl_3$ units in monolayer **3** can be used as structural motifs in the further construction of multilayer structures, since Cl ligands can be replaced by σ-

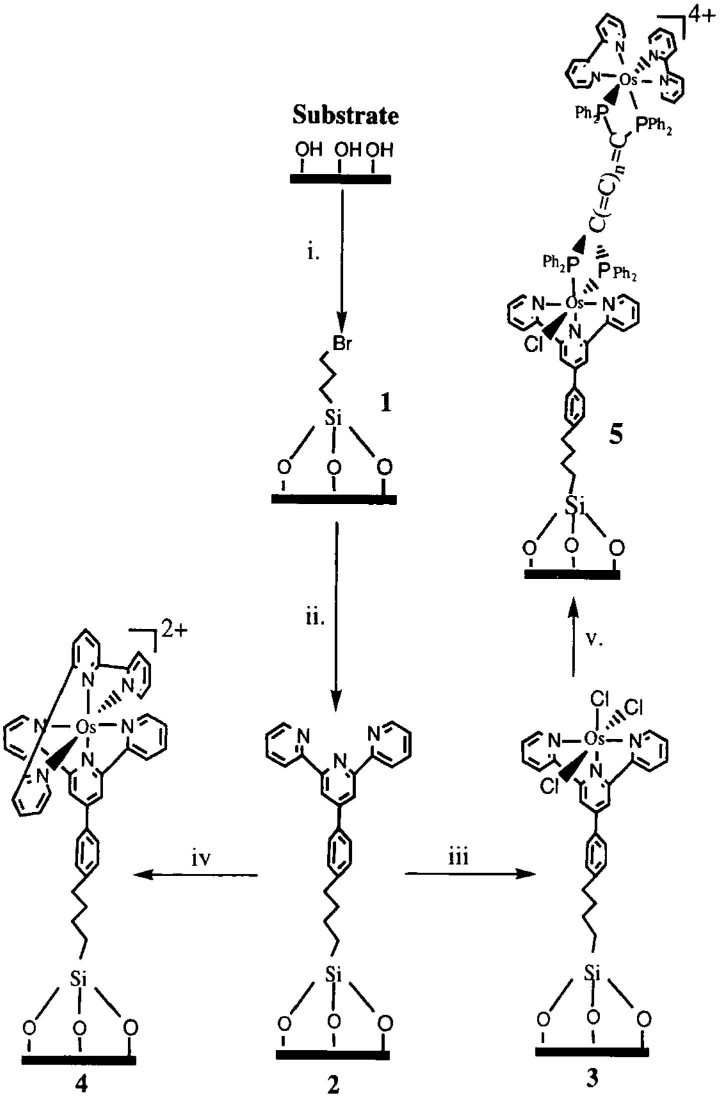


FIGURE 13 General procedures for covalent surface confinement of systems with sp carbon chains

or π-ligands, here the phosphine units. Step v shows a representative reaction of surface confined -$OsCl_3$ units with the second monometallic building block $Os(bpy)_2[(PPh_2)_2C(=C)_n=C(PPh_2)_2]$-$(PF_6)_2$, giving the bilayer thin film **5**.

6.2. UV-vis and XPS studies

Spectrophotometric changes are monitored during the surface treatment using UV/vis spectroscopy. Polycrystalline quartz has no significant absorption above 250 nm. Upon surface modification, typically we observe a small increase of absorption after attachment of -$Si(CH_2)_4$-Ph-tpy. Broad absorption bands at about 280 and 320 nm are observed upon addition of Os centers. The intensity of these two peaks increases as a function of reaction time and reaches maximum after three days, Figure 14. No significant increase or decrease in absorbance is observed after three days, indicating that a stable monolayer with terminal -CH_2-Ph-tpyOstpy units is obtained.

The calculation of surface coverage, using UV/vis spectroscopy, has also been carried out. Using the lowest energy π-π* transition at 280 nm, the estimated values of monolayer surface coverage for modified surfaces with terminal -CH_2-Ph-tpyOstpy ($\varepsilon_{s,280} = 2.8 \times 10^7$ cm^2 mol^{-1}) and - CH_2-Ph-tpy$OsCl_3$ ($\varepsilon_{s,280} = 1.2 \times 10^7$ cm^2 mol^{-1}) units are 2.0×10^{-10} and 3.6×10^{-10} mol cm^{-2}, respectively.[38] These values are comparable with the reported values (typically, 1×10^{-10} mol cm^{-2}) of the surface coverage for monolayers with Fe, Ru, or Re complexes.[34,35] The estimated surface coverage for bilayer with -CH_2-Ph-tpyOsCl-$[(PPh_2)_2C=C=C(PPh_2)_2]$-$Os(bpy)_2$ ($\varepsilon_{s,280} = 4.4 \times 10^7$cm^2 mol^{-1}) units is 2.7×10^{-11} mol cm^{-2}.

We have also monitored each surface modification step by studying the modified surfaces with X-ray photoelectron spectroscopy (XPS).[38,47] The elements involved in our modification procedures have their characteristic binding energies which can be clearly identified.[38] The successful covalent attachment of Os-based chromophores on quartz surface is verified by the observation of Os 4f at 53.85 eV ($4f_{7/2}$) and 56.45 eV ($4f_{5/2}$) for sample **3** as well as 53.80 eV ($4f_{7/2}$) and 56.40 eV ($4f_{5/2}$) for sample **4**, all of which are characteristic of the Os 4f peaks.[38] Upon further addition of the $Os(bpy)_2[(PPh_2)_2C=C=C(PPh_2)_2]$ unit, the observed Os 4f peaks in sample **5** shifted to slightly lower ener-

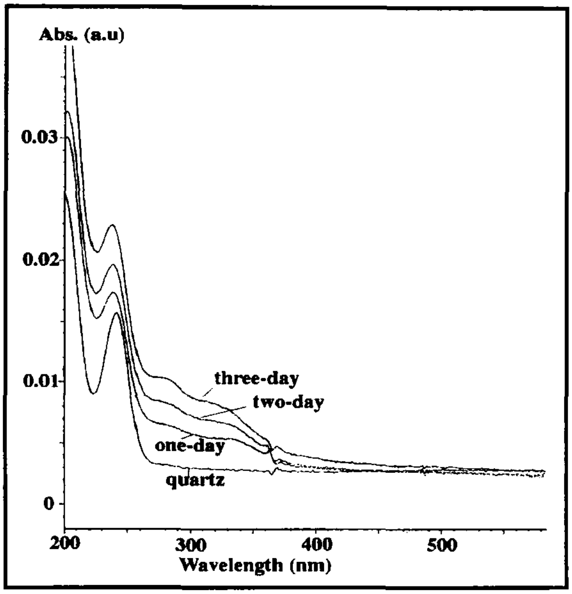


FIGURE 14 UV/vis study of monolayer with terminal -CH_2-Ph-tpyOstpy units after 1–3 days reaction

gies, with 53.30 and 55.90 eV for $4f_{7/2}$ and $4f_{5/2}$, respectively. Since there are both Os(III) and Os (II) centers in **5** and the reported energies of 4f peaks of Os(II) is slightly lower than those of Os(III) (i.e., with the same types of ligands, $4f_{7/2}$ is about 50.2 - 50.8 eV in $Os^{II}Cl_2(PhPMe_2)_4$ and about 51.4 – 52.0 eV in $Os^{III}Cl_3(PhPMe_2)_3$[48]), the small shift of Os 4f peaks in **5** towards the lower energy region may, partly, due to the overlapping Os 4f peaks of both Os(II) and Os(III) centers.

7. CONCLUDING REMARKS AND PERSPECTIVES

The rigid multicomponents supramolecular systems with cumulenic and acetylenyl bridges can be constructed from the di- and tetratopic spacers and various metal-based molecular precursors. With the use of suitable

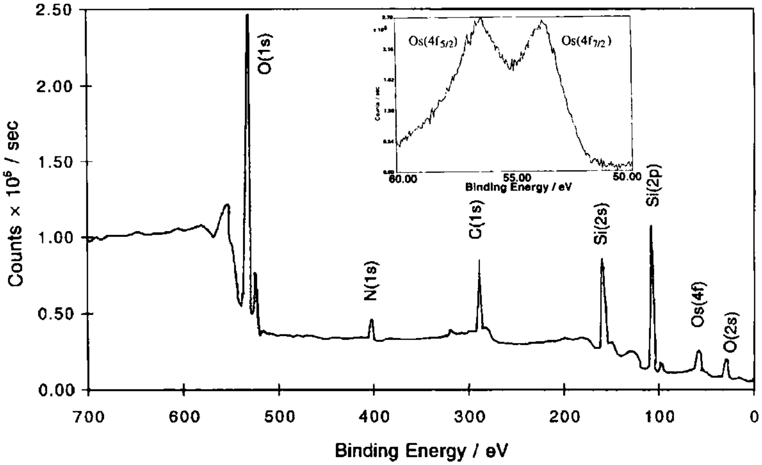


FIGURE 15 XPS Spectra of modified surface with attached -Si-$(CH_2)_4$-Ph-tpy-Os-tpy after a three-day reaction (Inset: high resolution scan of Os 4f region)

pre-assembled moieties and stepwise synthetic approaches, we can assemble a variety of supramolecular systems with systematic variation of nuclearity and distances between molecular subunits. As a result, the size and shape of molecules can be readily controlled, and the electrochemical and photophysical properties of these molecules systematically modulated.

Preparation of advanced multicomponent supramolecular systems with rigid sp carbon chain spacers not only poses great challenges on the synthetic methodologies, but also on the subsequent characterization and structural identification of the desired complexes. Currently our methods for characterization of spacers and their corresponding supramolecular systems are primarily NMR (^1H, ^{13}C, and ^{31}P) and mass spectral analysis. In addition to the two methods, namely, FAB/MS and MALDI-TOF/MS, that we have successfully employed, electrospray mass spectroscopy (ESI/MS) will also be a suitable candidate to study the new molecular rods and squares with up to 8+ charges and relatively high molecular weights (e.g., 5036 Da for $[Os(bpy)_2(C_8P_2)]_4(PF_6)_8]$. Recently we have successfully employed ESI/MS in the study of highly charged (8+) dendritic supramolecular system with silsesquioxane centers (representative molecular weight: 5337 Da).[49] Moucheron and Mesmarker[50] have also conducted the ESI/MS study of a dendritic heptanuclear Ru(II) complex. For supramolecular systems with multiple metal centers, relatively high molecular weights (>2 000 Da), and high charges, both MALDI-TOF/MS and ESI/MS, in addition to FAB/MS, will be extremely useful tools in structural identification and characterization.

In addition to above analyses, it will be valuable to carry out X-ray structure determination of new supramolecules in cases where crystals of suitable quality can be obtained. Important parameters such as cavity size and distance between the subunits on both ends of the carbon chains can be obtained. An alternative way to identify these important structural parameters is molecular modeling study. Such study is extremely useful when we cannot obtain single crystals of suitable quality for X-ray structure determination. The preliminary molecular modeling study (Insight/Discover in Biosym/MSI) of $[Os(bpy)_2(\mathbf{C_nP_4})Ru(bpy)_2]^{4+}$ have been conducted, and the Ru-to-Os distance is found to be 8.68 Å for n = 3 and 9.87 Å for n = 4.

The rate constants of electron/energy transfer are expected to decrease with increasing metal-to-metal distance R in heterometallic systems with sp carbon chains.[10,23–26,41] Such a distance dependence can be described as: $k = A \exp[-\beta R]$,[10] where β is the attenuation factor and k is the experimental rate constant of energy/electron transfer. For the bimetallic Ru/Os system with $tpy(C{\equiv}C)_n tpy$ (n = 2,4; tpy = 2,2':6',2"-terpyridine) bridges, the β value is evaluated by Harriman and Ziessel[10b] as 0.17±0.04 $Å^{-1}$. This value is relatively small when compared with that of aromatic hydrocarbons (0.4 $Å^{-1}$) or fused alkanes (0.6–1.0 $Å^{-1}$).[23d] Our current work will explore the similarity and differences in β values in systems containing ditopic and tetratopic polyphosphine spacers with cumulenic or acetylenyl bridges.

Molecular photophysics of our new supramolecular systems with sp carbon chains can be further extended, from the investigation of steady-state and time-resolved emission and absorption studies, to the study of molecular recognition based on changes in luminescence characteristics and NMR chemical shifts. The counterions in charged systems and solvents with different sizes, aromaticity, polarity, and electron donating ability will play a role in determining NMR chemical shifts and luminescence characteristics (such as relative luminescence intensities, excited state lifetimes, and emission maxima) of our supramolecular systems. Such properties are important to the possible applications of these photoresponsive macrocyclic systems in host-guest chemistry, molecular recognition, and sensing technologies.

Acknowledgments

The research carried out in the author's laboratory is supported by University of California, Irvine (including UCI startup Funds, UCI School of Physical Sciences Committee on Research grants, and UCI Faculty Career Development Award Program), the Petroleum Research Fund (administrated by the American Chemical Society), California Energy Institute (through Energy Science and Technology Program), National Science Foundation (CHE-9709693), and NSF-CAREER Award (CHE-9733546). The author would like to thank the following students whose commitment has made possible the joint contribution in the field of photoresponsive and redox-active supramolecular systems: graduate students Jeffrey V. Ortega, Dengfeng (Dennis) Xu, Hunter J. Murfee, Travis P. S. Thoms, Steven R. Woodcock, and Kimberly D. Edwards; undergraduate students Daniel G. Nunéz, Kay Khin, Jadelyn Chun, Sylvia K. Saito, and Michael J. Lebrun; and Dr. Mai Zhou. Acknowledgment is also made to financial support to student research in the author's laboratory, including UCI President's Undergraduate Fellowship Program, UCI Undergraduate Research Opportunity Program, California Alliance for Minority Participation (funded by National Science Foundation), Graduate and Professional Opportunity Program from Department of Education. The author thanks Professor John C. Hemminger at UCI Chemistry Department for the XPS measurements of surface-confined Os complexes, and Professor Wayne E. Jones, Jr. at State University of New York at Binghamton for the measurement of short lifetimes of **RuC_nOs**(n = 3, 4) on frequency domain fluorimeter. The author also thanks Dr. Wytze van der Veer (UCI Laser Facility) and Dr. John Greaves (UCI Mass Spectral Laboratory) for their assistance in the measurements of time-resolved absorption and emission, and mass spectral studies.

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