Photophysical Studies of Metal to Ligand Charge Transfer Involving Quadruply Bonded Complexes of Molybdenum and Tungsten

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Malcolm H. Chisholm,* Samantha E. Brown-Xu, and Thomas F. Spilker

Department of Chemistry and Biochemistry The Ohio State University Columbus, Ohio 43210, United States

CONSPECTUS: Photoinduced metal-to-ligand charge transfer transitions afford numerous applications in terms of photon energy harvesting. The majority of metal complexes studied to date involve diamagnetic systems of d^6, d^8, and d^{10} transition metals. These typically have very short-lived, ~100 fs, singlet metal to ligand charge transfer (^{1}MLCT) states that undergo intersystem crossing to triplet metal to ligand charge transfer (^{3}MLCT) states that are longer lived and are responsible for much of the photophysical studies. In contrast, the metal−metal quadruply bonded complexes of molybdenum and tungsten supported by carboxylate, O_2CR, and related amidinate ligands $(RN)_2C(R')$ have relatively long-lived ^{1}MLCT states arising from $M_2\delta$ to $L\pi^*$ transitions. These have lifetimes in the range 1−20 ps prior to intersystem crossing to T_1 states that may be ^{3}MLCT or ^{3}MM$\delta\delta^*$ with lifetimes of 1−100 ns and 1−100 μs, respectively. The M_2 quadruply bonded complexes take the form M_2L_4 or $M_2L_{4-n}L'_n$ where n = 1−3. Thus, in their photoexcited MLCT states, these compounds pose the question of how the charge resides on the ligands.

M = Mo or W

This Account reviews the current knowledge of how charge is positioned with time in S_1 and T_1 states with the aid of active IR reported groups located on the ligands, for example, $C\equiv X$ multiple bonds (X = C, N, or O). Several examples of localized and delocalized charge distributions are noted along with kinetic barriers to the interconversion of MLCT and $\delta\delta^*$ states. On the 50th anniversary of the recognition of the MM quadruple bond, these complexes are revealing some remarkable features in the study of the photophysical properties of metal−ligand charge transfer states.
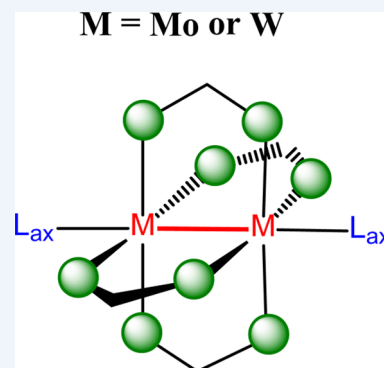
INTRODUCTION

The year 2014 marks the 50th anniversary of the recognition of the metal−metal quadruple bond.[1,2] Since that time, well over a thousand related quadruply bonded complexes have been isolated and hundreds structurally characterized by single crystal X-ray studies largely as a result of the work of Cotton and his co-workers.[3] In 1964, the quadruple bond was a bond of uniquely high order, exceeding those of triple bonds, which were well recognized involving the first row elements carbon, nitrogen, and oxygen. A characteristic feature of these quadruply bonded complexes is the existence of a 4-fold rotational axis along the M−M bond. For a d^4−d^4 transition metal complex, as in $Re_2Cl_8^{2-}$, this leads to the now well accepted ordering of MM bonding orbitals, $\sigma^2\pi^4\delta^2$. A prominent class of complexes involves the presence of carboxylates that form bridges across the MM bond and enforce the eclipsed geometry. Related classes of ligands, where one or both of the carboxylate oxygen atoms are substituted by the isoelectronic atom S or group NR, similarly span the MM bond forming five-membered rings and introduce ligand π and π^* orbitals that can interact with the $M_2\delta$ orbital. These compounds of general formula M_2L_4 where M = Mo or W are commonly referred to as paddle-wheel complexes (Figure 1).
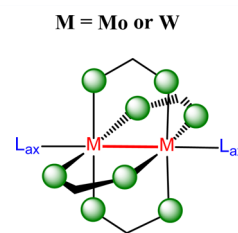

M = Mo or W

Figure 1. General structure of a M_2L_4 paddle-wheel compound (M = Mo or W).

Early studies of the photophysical properties of MM quadruply bonded complexes focused on the $\delta \rightarrow \delta^*$ transition.[3−5] The intensity of this transition is relatively weak with ε values of ~100 M^{-1} cm^{-1} due to the poor d−d overlap in a δ orbital. In contrast, with the use of π-accepting ligands (carboxylates, amidinates, thiocarboxylates, etc.), the $M_2\delta$ to $L\pi^*$ transition is a fully allowed metal-to-ligand charge transfer (MLCT) and is much more intense with molar absorptivities from 10 000 to 140 000 M^{-1} cm^{-1}.[6] The $M_2\delta$ to $L\pi^*$ transition

can be tuned to fall in the range of 400−1200 nm by choice of metal and π-accepting ligand.[7,8]

These complexes typically show photoluminescence from both the S_1 and T_1 excited states. Time-resolved transient absorption spectroscopy on the femtosecond and nanosecond time scales has been used to measure the lifetimes of these states. In general, the ^{1}MLCT S_1 states have lifetimes of 1−20 ps.[6] This is true for all carboxylates, formamidinates, and amidinates, and even the replacement of N or O by the heavier element S has little influence on the lifetime of the ^{1}MLCT state. The lifetimes for W_2-containing compounds are comparable to their Mo_2 analogues. Interestingly the S_1 states that are ^{1}MoMo$\delta\delta$* in character have notably longer lifetimes, ~70 ps.[9] Lifetimes of ^{3}MM$\delta\delta$* states fall in the range 1−100 μs and are unaffected by the nature of the ligand, though they are shorter for M = W than for M = Mo. The ^{3}MLCT states of W_2 compounds are typically shorter lived, approximately 1−10 ns.[6]

Compared with the majority of transition metal complexes, the lifetimes of these ^{1}MLCT states are exceptionally long. For example, Ru(bpy)$_3^{2+}$ has a ^{1}MLCT state that undergoes intersystem crossing, ISC, within 50 fs[10] and Pt(II) acetylide S_1 states are similarly short-lived.[11] These quadruply bonded complexes thus afford the opportunity of examining the charge distribution with time in both singlet and triplet states using time-resolved infrared (TRIR) spectroscopy. Our initial efforts in this area have been based on the attachment of ligands bearing C≡X units where the value of ν(C≡X) falls in the region 2250−1850 cm^{-1}, which is well-separated from lower energy vibrations. We have thus far examined examples of M_2 containing compounds bearing one, two, or four such π-acceptor ligands.

Complexes having two or more ligands with relatively low-lying π* molecular orbitals pose the question of the location of charge in the MLCT states. The charge could be localized on one ligand or delocalized equally over both Lπ* acceptors. These can be described in terms of excited state mixed valence[12] where a localized charge represents valence trapped or class I behavior on the Robin and Day[13] classification while a delocalized situation represents class III behavior. Furthermore, the location of charge may change with time and may differ in the singlet and triplet states. The properties of a ligand in a MLCT state correspond closely to those of the reduced ligand, and as such, electronic structure calculations on the ground state and the anion, that is, M_2L_4 and $[M_2L_4]^-$, can be useful. The molecular orbital calculations will in general favor a delocalized bonding model, so ν(C≡X) calculated for the anion compared with the experimentally observed vibration in the MLCT states can form a useful starting point in assigning the degree of charge delocalization.

ELECTRONIC STRUCTURE OF MM COMPLEXES

The general molecular orbital energy diagram shown in Figure 2 applies to homoleptic complexes of the form M_2L_4 and shows the fundamental composition of the quadruple bond. In addition to the σ, π, δ, δ*, π*, and σ* MM based orbitals, the presence of the four carboxylates introduces ligand π and π* orbitals, which in the point group D_{4h} transform as e_u, b_{2g}, and a_{2g}. Depending upon the extent of π-conjugation, the energy of the δ* and carboxylate π* are close and promotion of an electron from the filled δ orbital to the e_u orbital is a fully allowed MLCT transition. In complexes with extended π-conjugation, the $\delta \rightarrow \pi$* HOMO to LUMO electronic transition completely masks the $\delta \rightarrow \delta$* transition, which is
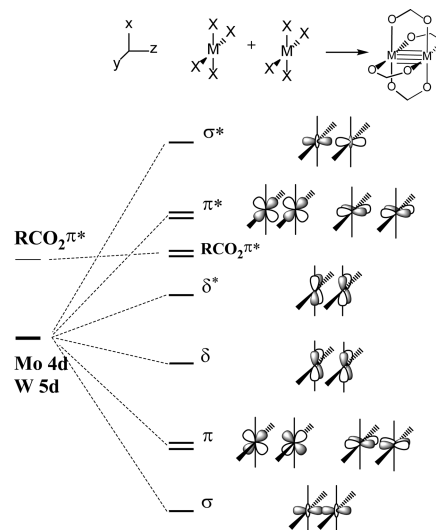

Figure 2. Generalized frontier molecular orbital energy level diagram for a $Mo_2(O_2CR)_4$ compound.

most often higher in energy. The energy of this $\delta \rightarrow \pi$* transition is tunable by choice of metal (Mo or W) since the $W_2\delta$ orbital lies roughly 0.5 eV higher in energy relative to its Mo_2 counterpart. The transition is also affected by the energy of the Lπ* orbital, which falls as the CO_2 unit is brought into conjugation with π-accepting substituent such as -CN and -NO$_2$.

By far the largest group of complexes studied have been the bis−bis complexes derived from the homoleptic complexes. Specifically, they are prepared from the reaction of a homoleptic precursor, most often $M_2(T^iPB)_4$ (M = Mo, W; T^iPB = 2,4,6-triisopropylbenzoate),[14,15] with two equivalents of the appropriate carboxylic acids, LH. Carboxylates attached to the M_2^{4+} quadruply bonded centers are kinetically labile to ligand scrambling; however, it is possible to prepare and isolate pure *trans*-MM(T^iPB)$_2L_2$ compounds with the use of the bulky T^iPB ligands.[16] The trans-substitution is favored on steric grounds and by the extended Lπ−$M_2\delta$−Lπ conjugation.[17] In the ground state, the aryl rings of the T^iPB ligands are twisted ~90° from the planes of their respective carboxylate groups forcing them out of conjugation with the $M_2\delta$ orbital.

A simple frontier molecular orbital interaction diagram is shown in Figure 3. Based on orbital energetics, it is the Lπ* orbital interaction that is favored with the $M_2\delta$ orbital. As shown, only the out-of-phase Lπ* combination can interact with the $M_2\delta$. This leads to a splitting of the two ligand π* systems, and the energy of this splitting is a rough measure of the coupling of the two Lπ ligands via the dimetal center. In certain cases, reduction of these complexes can lead to ligand based radical anions that are fully delocalized, class III on the Robin and Day scheme.[18]

Amidinate ligands (RN)$_2$C(R′), where R = alkyl or aryl and R′ = H or a functional organic group, are kinetically more persistent and allow for alternative substitution patterns to be prepared. These include M_2^{4+} centers bearing one carboxylate π* acceptor ligand and three amidinate ancillary ligands, as well as bis-amidinate, bis-carboxylate complexes with either a trans or cis geometry. The orbital interactions for cis complexes are such that only one ligand π* orbital combination can interact with the $M_2\delta$ orbital, similar to those for the trans compounds depicted in Figure 3.
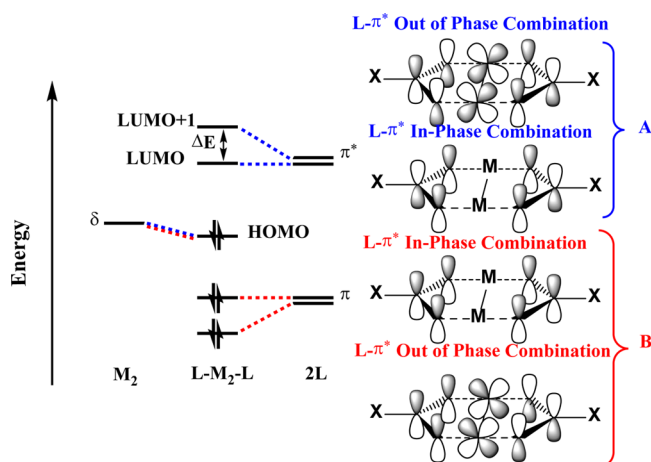
Figure 3. Frontier molecular orbital interactions involving *trans*-L−M₂−L complexes.

The relative ordering of the singlet and triplet excited states is significantly influenced by the metal and the coordinating ligands. Upon photoexcitation, the tetracarboxylate complexes show weak fluorescence from their ¹MLCT states and undergo intersystem crossing to triplet states that may be either ³MLCT or ³MMδδ*. With nonconjugated ligands, such as in M₂(TⁱPB)₄, the T₁ state is ³MMδδ*, and the phosphorescence follows the energy order W₂ > WMo > Mo₂ with emission occurring at ∼800 nm for W₂ complexes and at ∼1100 nm for Mo₂ complexes.[19] At low temperatures, the ³MMδδ* emission typically shows vibronic features spaced by 300−400 cm⁻¹ associated with ν(MM) in the ground state (Figure 4).[20] The
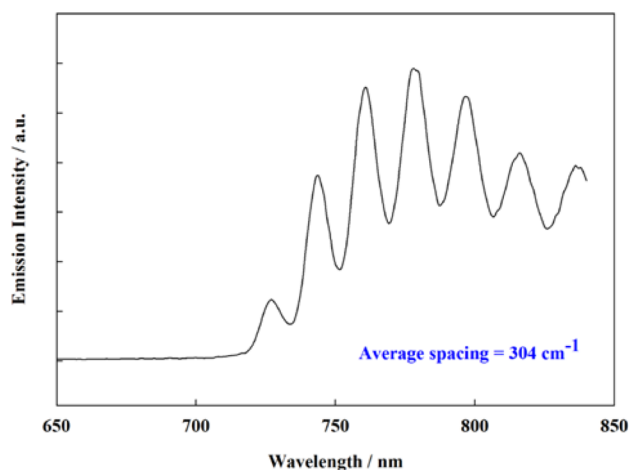

Figure 4. Phosphorescence energy from the ³WWδδ* state of W₂(O₂CC≡CMe)₄ in 2-MeTHF at 77 K.

energies of these δδ* states are relatively insensitive to the nature of the carboxylate substituents. Extension of the ligand π-conjugation lowers the Lπ* levels, and consequently the energies of the ¹MLCT and ³MLCT states decrease. For W₂ complexes, this results in a ³MLCT T₁ state, whereas in the case of Mo₂, the T₁ state most often remains ³MoMoδδ*.

For complexes with amidinate-type ligands ((RN)₂C(R′), R = aryl or alkyl and R′ = H or aryl) the MLCT states are at higher energy because of the higher relative energies of the NCNπ* orbitals compared with CO₂π*. In addition, the filled N p nonbonding orbitals are higher in energy and are able to

more strongly interact with the M₂ δ and δ* orbitals, raising them in energy. Ultimately this results in the MMδδ* levels being destabilized relative to their carboxylate counterparts.[2] The energy of the MLCT state can be lowered in amidinates, where L = (RN)₂C(R′) and R′ = C≡C−Ar, because the R′ group is now brought into conjugation with the NCN π system.[9] In cases of mixed amidinate−carboxylate complexes in which the lowest energy transition is from M₂δ to carboxylate Lπ*, the ancillary amidinate ligands have the effect of elevating the MMδδ* states, while the low energy carboxylate Lπ* orbitals depress the MLCT states. The combination of these two effects makes it possible to invert the typical triplet state ordering found in Mo₂ complexes such that the T₁ state is instead ³MLCT.[21]

■ TIME-RESOLVED INFRARED STUDIES

Bis−Bis Complexes

Bis−bis complexes containing a wide variety of π-acceptor ligands with -C≡X functional groups have now been studied by femtosecond time-resolved infrared (TRIR) spectroscopy. One of the primary interests in this area is the determination of the excited state charge distribution. In many of the transition metal polypyridyl and Pt(II) acetylide complexes, the excited electron has been found to rapidly localize on one ligand.[22] In the numerous dimetal complexes studied, examples of both fully delocalized class III and localized class I excited state mixed valence have been observed. The shift of the reporter group vibration, ν(C≡X), in the excited states relative to the ground state has been used as an indicator of charge localization or delocalization. Delocalized cases have in fact been found to be more prevalent, and these examples will be presented first.

Several compounds of the form M₂TⁱPB₂L₂ where L = O₂C-R and R contains a -C≡C- or -C≡N group have been studied. The fs-TRIR spectra for the compounds *trans*-M₂(TⁱPB)₂(O₂CC₆H₄-4-CN)₂ are shown in Figure 5.[23] For both M = Mo and W, we observe a bleach of the ground state -C≡N vibration at ∼2230 cm⁻¹ and a single transient band shifted 60 cm⁻¹ to lower energy that is assigned to ν(C≡N) in the ¹MLCT state. For M = Mo, this transient IR band is lost following ISC to the metal-centered ³δδ* state. However, for M = W, the T₁ state is ³MLCT and the ν(C≡N) band remains present at 3 ns.

Bis−bis compounds bearing 5-ethynylthiophene-2-carboxylate ligands, *trans*-M₂(O₂CH)₂(O₂CThC≡C−H)₂,[24] show similar results in their TRIR spectra. For both M = Mo and W, there is a single transient -C≡C- vibration in the ¹MLCT state shifted −66 and −52 cm⁻¹ from the ground state, respectively. Upon intersystem crossing, the Mo₂ compound shows no vibrations in the region of ν(C≡C), whereas for W₂ there is a long-lived feature shifted −68 cm⁻¹ relative to the ground state.

In these cases, the presence of a single -C≡N or -C≡C-stretch in the excited state together with the similar value of Δν(C≡X) compared with that calculated for the anions *trans*-M₂(O₂CH)₂(O₂CC₆H₄-4-CN)₂⁻ and *trans*-M₂(O₂CH)₂(O₂CThC≡C−H)₂⁻ are indicative of charge delocalization over both π-accepting ligands in the MLCT states. This situation is commonly observed for complexes of the form *trans*-M₂(TⁱPB)₂L₂ and several examples with their TRIR data are listed in Table 1.
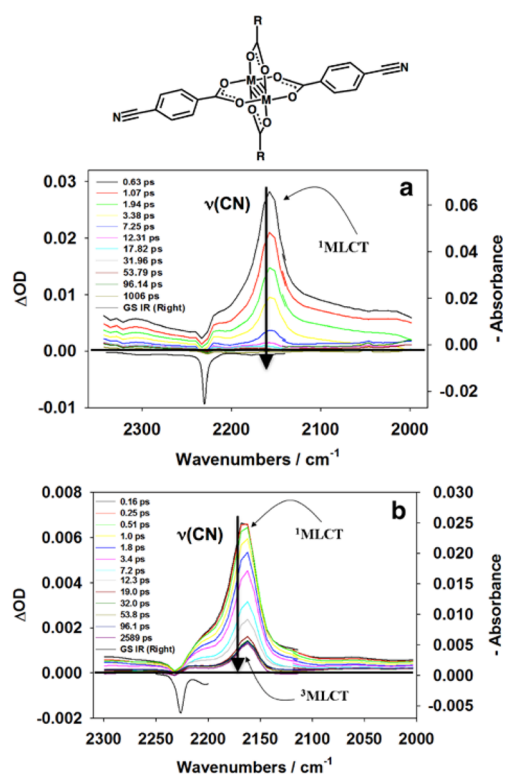
Figure 5. Femtosecond TRIR spectra of the complexes $M_2(T^iPB)_2(O_2CC_6H_4\text{-}4\text{-}CN)_2$ collected in THF at RT: (a) M = Mo, λ_{ex} = 515 nm; (b) M = W, λ_{ex} = 675 nm (adapted from ref 23).

As a means of comparison, we have also examined the fs-TRIR of complexes with just one low energy π-acceptor ligand, namely, $Mo_2(DAniF)_3L$, where DAniF = N,N'-di(p-anisyl)-formamidinate and L = $O_2CC_6H_4\text{-}4\text{-}CN$, $O_2CC\equiv CPh$, and $O_2CThC\equiv C\text{-}H$, Figure 6.[25] Here in the lowest energy ^1MLCT state, the negative charge is necessarily localized on just one ligand, and as such the values of $\Delta\nu(C\equiv X)$ can be related with those of the corresponding $trans$-$Mo_2(T^iPB)_2L_2$
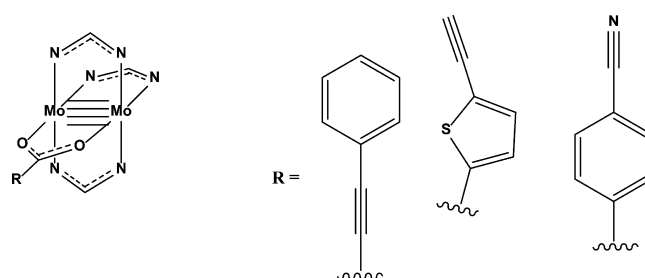

Figure 6. General structure of complexes of the form $Mo_2(DAniF)_3(O_2C\text{-}R)$.

complexes. As shown in Table 1, the magnitude of $\Delta\nu(C\equiv X)$ is larger in these monocarboxylate complexes and is roughly twice that of the complexes that have been assigned as delocalized, though a rigorous comparison is not valid since the ancillary ligands are different.

In contrast, the fs-TRIR spectra of the complexes $trans$-$M_2(O_2CMe)_2[(Pr^iN)_2CC\equiv CPh]_2$, where the amidinate ligands are the lowest energy π^* acceptors, are very different (Figure 7).[23] Here two $\nu(C\equiv C)$ vibrations are seen for the ^1MLCT states for both M = Mo and M = W. The more intense band appears 200–240 cm^{-1} to lower energy relative to the ground state, while a band of lesser intensity is shifted by only 40 cm^{-1}. Calculations on the anions $trans$-$M_2(O_2CMe)_2[(Pr^iN)_2CC\equiv CPh]_2^-$ predict a single $\nu(C\equiv C)$ shifted ~120 cm^{-1} to lower energy. Thus, the appearance of two -C≡C- vibrations in the ^1MLCT state, together with the magnitude of the observed $\Delta\nu(C\equiv C)$ provides clear evidence of a nondelocalized distribution of charge. Indeed, the magnitude of the shifts suggests that the charge rests largely on one ligand with just a small "spillover" onto the other arm.

Again for M = Mo, the T_1 state is $^3 MoMo\delta\delta^*$ and is silent in the C≡C region of the spectra. However, for M = W, new IR bands for $\nu(C\equiv C)$ in the ^3MLCT T_1 state grow in as ISC occurs. Most interestingly, these are shifted even further from the ground state indicating a different charge distribution in the ^3MLCT state. The lower $\nu(C\equiv C)$ frequencies indicate a

Table 1. Ground and Photoexcited State Infrared Active C≡X Stretching Frequencies Selected Quadruply Bonded Complexes[a]

compound			IR $\nu(C\equiv X)$, cm^{-1}			
formula	L	L'	ground state	S_1 ($\Delta\nu$)	T_1 ($\Delta\nu$)	ref
Mo_2L_4	$O_2CC_6H_4\text{-}4\text{-}CN$		2230	2220 (−10), 2158 (−72)	2235 (+5)[d]	28
Mo_2L_4	$O_2CC_6H_4\text{-}4\text{-}C\equiv CH$		2105	2044 (−61)	f	28
$trans$-W_2L_2L'	$O_2CC\equiv CPh$	T^iPB[b]	2200	2125 (−75), 1975 (−225)	2000 (−200)[e]	29
$trans$-W_2L_2L'	$O_2CC\equiv CAn$	T^iPB[b]	2200	2150 (−50)	f	29
$trans$-Mo_2L_2L'	$O_2CC_6H_4\text{-}4\text{-}CN$	T^iPB[b]	2230	2157 (−73)	f	23
$trans$-W_2L_2L'	$O_2CC_6H_4\text{-}4\text{-}CN$	T^iPB[b]	2225	2164 (−61)	2162 (−63)[e]	23
$trans$-Mo_2L_2L'	$O_2CThC\equiv C\text{-}H$	T^iPB[b]	2099	2033 (−66)	f	24
$trans$-W_2L_2L'	$O_2CThC\equiv C\text{-}H$	T^iPB[b]	2099	2047 (−52)	2031 (−68)[e]	24
$trans$-Mo_2L_2L'	$O_2CC_6H_5Cr(CO)_3$	T^iPB[b]	1977, 1908	1933 (−44), 1870 (−38)	1984 (+7), 1919 (+9)[d]	27
$trans$-W_2L_2L'	$O_2CC_6H_5Cr(CO)_3$	T^iPB[b]	1971, 1903	1935 (−36), 1873 (−30)	1930 (−41), 1853 (−50)[e]	27
$trans$-Mo_2L_2L'	$(PMT)Re(CO)_3Cl$	T^iPB[b]	2024, 1921, 1898	2009 (−15), 1902 (−19), 1890 (−18)	2027 (+3), 1923 (+2), 1901 (+4)[d]	26
$trans$-Mo_2L_2L'	$(Pr^iN)_2CC\equiv CPh$	O_2CMe	2200	2155 (−45), 1959 (−241)	f	23
$trans$-W_2L_2L'	$(Pr^iN)_2CC\equiv CPh$	O_2CMe	2180	2152 (−28), 1989 (−191)	2116 (−64), 1942 (−238)[e]	23
cis-$Mo_2L_2L_2'^-$	$O_2CThC\equiv CTh$	$DAniF$[c]	2197	2085 (−112)	f	30
Mo_2LL_3'	$O_2CC\equiv CPh$	$DAniF$[c]	2135	1975 (−240)	f	25
M_2LL_3'	$O_2CThC\equiv C\text{-}H$	$DAniF$[c]	2100	1970 (−130)	f	25

[a]Recorded in THF solutions at room temperature. [b]T^iPB = 2,4,6-triisopropylbenzoate. [c]N,N'-di(p-anisyl) formamidinate. [d]$^3MM\delta\delta^*$. [e]^3MLCT. [f]Not detected.
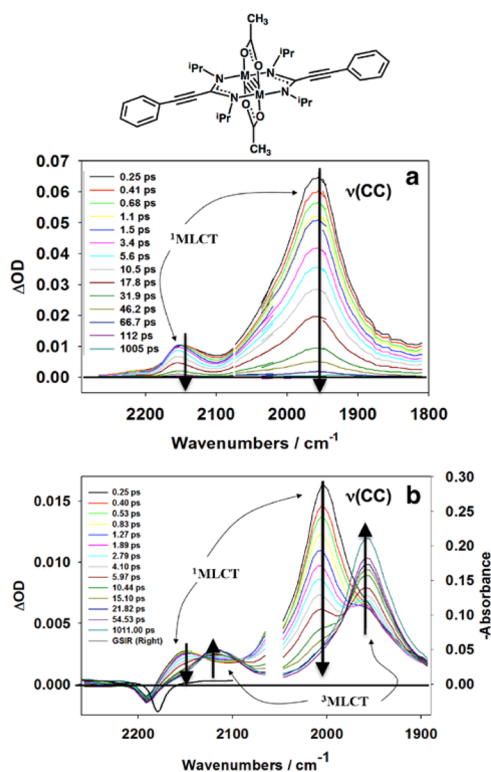
Figure 7. fs-TRIR spectra of the complexes $M_2(O_2CMe)_2[(Pr^iN)_2CC\equiv CPh]_2$ collected in THF at RT: (a) M = Mo, λ_{ex} = 515 nm; (b) M = W, λ_{ex} = 675 nm (adapted from ref 23).

greater concentration of charge in the -C≡C- π^* orbitals and suggest that in the lower energy T_1 state the ligand-centered charge is contracted toward the W_2 center yet still distributed unequally over both ligands, an example of class II behavior on the Robin and Day scheme.

A similar situation of charge localization is seen in the singlet and triplet MLCT states of the compound *trans*-$W_2(T^iPB)_2(O_2CC\equiv C$-tolyl$)_2$, though as of yet no other localized examples have been investigated.

Molecular Triads

Another class of trans bis—bis compounds has been studied that possess organometallic metal tricarbonyl units coordinated to the M_2 center to form molecular triad species. Metal carbonyl complexes were some of the first monitored by time-resolved infrared methods owing to the high oscillator strengths of the -C≡O vibrations, and this has proved a useful reporter group in our studies as well. The triads investigated have either rhenium[26] (*trans*-$Mo_2(T^iPB)_2[(PMT)Re(CO)_3Cl]_2$; PMT = 2-pyridyl-5′-methyl thiazolate) or chromium[27] (*trans*-$M_2(T^iPB)_2[O_2CC_6H_5Cr(CO)_3]_2$; M = Mo, W) as the heterometal. The solid-state molecular structure of the Cr−Mo_2−Cr triad is shown in Figure 8.

The introduction of additional d orbitals from the secondary transition metal can cause a perturbation of the typical electronic structure. DFT calculations on the Mo_2-containing complexes indicate that the HOMOs are an admixture of $M_2\delta$ and a heterometal t_{2g}^6 orbital. However, oxidation of these triads with $AgPF_6$ gave species with EPR spectra characteristic of a δ^1 Mo_2^{5+} center.[26] For tungsten, the HOMO has mostly $W_2\delta$ character due to its higher energy and reduced mixing with the secondary metal d orbitals.
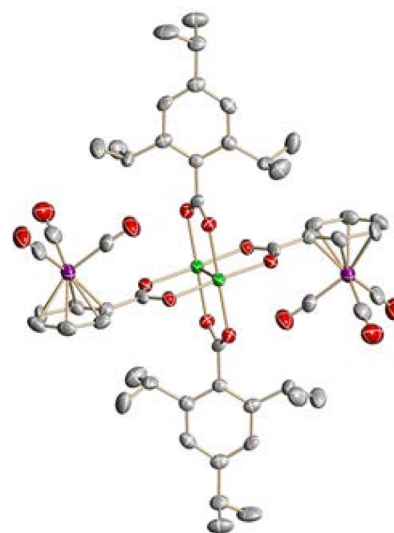

Figure 8. Molecular structure of the centrosymmetric $Mo_2(T^iPB)_2[O_2CC_6H_5Cr(CO)_3]_2$ molecule (adapted from ref 27).

The ground state IR spectra of the complexes have carbonyl vibrations at lower energy than the simple η^6-$C_6H_6Cr(CO)_3$ and $(PMT)Re(CO)_3Cl$ molecules consistent with ground state $M_2\delta$ to arene $L\pi^*$ back-bonding. Upon photoexcitation into the ^{1}MLCT states (λ_{ex} = 515 nm for Cr−Mo−Cr; 675 nm for Cr−W−Cr and Re−Mo−Re), the fs-TRIR spectra show $\nu(CO)$ bands shifted to lower energy consistent with negative charge being present on the arene rings (Figure 9). The shift in $\nu(CO)$ from the ground state was roughly half that predicted for the anions $HO_2CC_6H_5Cr(CO)_3^-$ and $(PMT-H)Re(CO)_3Cl^-$. Indeed, the observed $\Delta\nu(CO)$ values were close to those calculated for the anions *trans*-$[M_2(O_2CH)_2L_2]^-$, and the MLCT states were therefore assigned as delocalized over both π-ligands. The TRIR spectra recorded in the coordinating solvent THF for the complex *trans*-$Mo_2(T^iPB)_2[O_2CC_6H_5Cr(CO)_3]_2$ were more complex than those obtained in CH_2Cl_2 and were indicative of competitive reversible CO loss and Cr t_{2g}^6 to arene π^* charge transfer.[27]

Homoleptic Complexes

At this time, only two homoleptic compounds containing C≡X triple bonds have been studied by TRIR spectroscopy, namely, Mo_2L_4 where L = $O_2CC_6H_4$-4-CN and $O_2CC_6H_4$-4-C≡CH.[28] These are, however, very interesting when compared with the spectra noted above.

In D_{4h} symmetry, the $L\pi^*$ orbitals transform as a_{2g}, b_{2g}, and e_u. Of these, the b_{2g} orbital can mix with the $M_2\delta$ of like symmetry. The frontier molecular orbital energy level diagram for the $Mo_2(O_2CC_6H_4$-4-CN$)_4$ molecule is shown in Figure 10. That for the complex where L = $O_2CC_6H_4$-4-C≡CH is similar.

The HOMO−LUMO transition is a fully allowed MLCT, $b_{2g} \rightarrow e_u$. Thus, the ^{1}MLCT state will contain a single electron in a doubly degenerate orbital of e_u symmetry and as such will be subject to a Jahn−Teller distortion, though the JT theorem does not predict the nature of the distortion. The fs-TRIR spectra in the C≡X region are informative and are shown in Figure 11 for $Mo_2(O_2CC_6H_5$-4-CN$)_4$. The principal new $\nu(C\equiv N)$ band is shifted to lower energy by 70 cm^{-1}, but there is also a weaker $\nu(C\equiv N)$ shifted only −8 cm^{-1} relative to the ground state. By comparison with the related fs-TRIR of the *trans*-$Mo_2(T^iPB)_2(O_2CC_6H_4-CN)_2$ complex, the shift in $\nu(C\equiv N)$ is similar. This leads us to propose that the charge
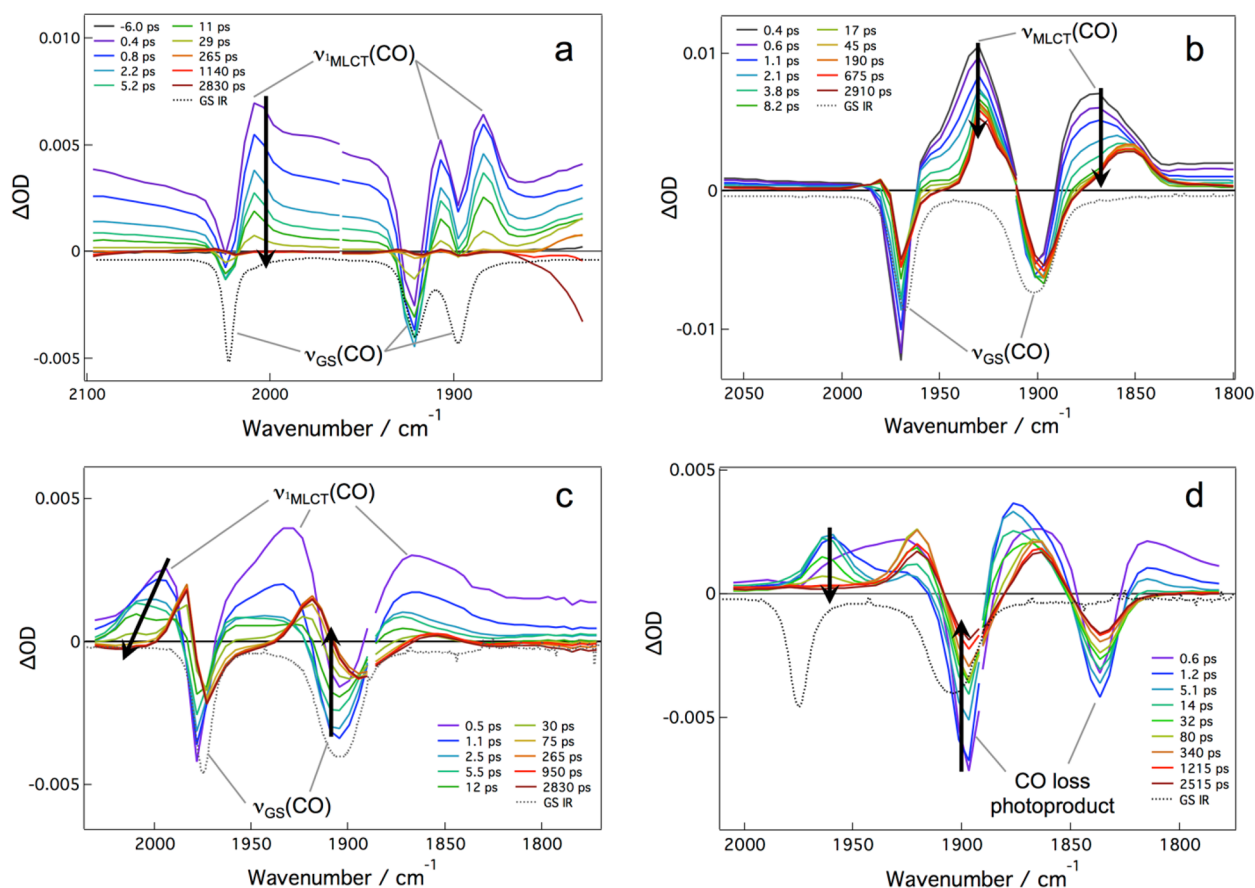
Figure 9. fs-TRIR spectra of (a) *trans*-Mo$_2$(T^{i}PB)$_2$[(PMT)Re(CO)$_3$Cl)]$_2$ in THF/DMSO at RT, λ_{ex} = 675 nm,[26] (b) *trans*-W$_2$(T^{i}PB)$_2$[O$_2$CC$_6$H$_5$Cr(CO)$_3$]$_2$ in THF at RT, λ_{ex} = 675 nm, (c) *trans*-Mo$_2$(T^{i}PB)$_2$[O$_2$CC$_6$H$_5$Cr(CO)$_3$]$_2$ in CH$_2$Cl$_2$ at RT, λ_{ex} = 515 nm, and (d) *trans*-Mo$_2$(T^{i}PB)$_2$[O$_2$CC$_6$H$_5$Cr(CO)$_3$]$_2$ in THF at RT, λ_{ex} = 515 nm. Panels a and c show the appearance of ν(CO) in the ^{1}MLCT and ^{3}MoMo$\delta\delta$* states, while (b) shows $^{1/3}$MLCT states. Spectra in panel a adapted from ref 26; panels b−d adapted from ref 27.

is largely distributed over two trans O$_2$CC$_6$H$_4$-4-CN ligands with just a small "spillover" to the other two orthogonal ligands. After decay to the ^{3}MoMo$\delta\delta$* state, these features are lost but there remains a long-lived (>3 ns) ν(C≡N) band roughly 5 cm^{-1} higher than the ground state value. In the triplet state, one electron is removed from the δ orbital, which weakens the back-bonding to the Lπ* acceptor ligands.

Detection of the $\delta\delta$* States

As noted earlier, the ^{1}MLCT states often lie lower in energy than the $^1\delta\delta$* states. However, in certain complexes such as M$_2$(O$_2$CBu^t)$_4$ and Mo$_2$(DAniF)$_3$(O$_2$CBu^t), it is possible to detect the $^1\delta\delta$* state by both fs-TA and fs-TRIR spectroscopy.[9,25] The fs-TRIR spectra associated with the compound Mo$_2$(DAniF)$_3$(O$_2$CBu^t) recorded in THF with irradiation into the Mo$_2\delta$ to CO$_2\pi$* transition are illustrative of these features and are shown in Figure 12.[25]

Upon formation of the ^{1}MLCT state, we observe bleaches of ν_{as}(CN$_2$) and ν_{as}(CO$_2$) at 1540 and 1500 cm^{-1}, respectively. The ν_{as}(CO$_2$) is reduced to 1490 cm^{-1}, and a weak signal assignable to ν_{as}(CN$_2$) occurs at slightly higher energy relative to the ground state. This is understandable because the filled N p$_\pi$ orbitals mix with the Mo$_2\delta$ in the HOMO so that the formamidinate ligands participate to some extent in the Mo$_2\delta$ to CO$_2\pi$* charge transfer. This state has a lifetime of 2 ps before internal conversion to the close in energy S$_1$ ^{1}MoMo$\delta\delta$* state, indicated by the shift of ν_{as}(CO$_2$) and rise of a ν_{as}(CN$_2$) band to lower energy from the ground state.

The metal-centered S$_1$ state has a surprisingly long lifetime, 70 ps, and decay to the ^{3}MoMo$\delta\delta$* state is evidenced by the growth of ν_{as}(CN$_2$) at 1560 cm^{-1}, while ν_{as}(CO$_2$) again shifts to higher energy. Evidently in these mixed amidinate−carboxylate complexes, it is the ν_{as}(CN$_2$) that shifts to higher energy rather than ν_{as}(CO$_2$) as seen in Mo$_2$(O$_2$CBu^t)$_4$.[9] This is supported by predictions from DFT calculations on the S$_0$ and T$_1$ states and likely reflects the greater mixing of the Mo$_2\delta$ and filled N p$_\pi$ orbitals.[25]

In other dimolybdenum complexes, it is possible for the ^{3}MLCT state to lie lower in energy than the ^{3}MoMo$\delta\delta$* state, as observed in Mo$_2$(DAniF)$_3$(O$_2$C-anthroquinone). Here one can detect the higher energy ^{3}MoMo$\delta\delta$* state by ns-TA, which is notably shorter lived ($\tau \approx$ 100 ns) compared with the more usual lifetime of ∼50 μs when no low energy ^{3}MLCT state is present. The persistence of the ^{3}MoMo$\delta\delta$* state implies a kinetic barrier for the internal conversion within the triplet manifold.[21]

The unusually slow rates of internal conversion and intersystem crossing observed in these compounds indicate larger kinetic barriers to the decay processes and warrant further investigation.

■ CONCLUDING REMARKS

The M$_2\delta$ orbital has the appropriate symmetry to allow for conjugation with ligand π and π* orbitals in carboxylate, formamidinate, and amidinate ligands attached to the M$_2$
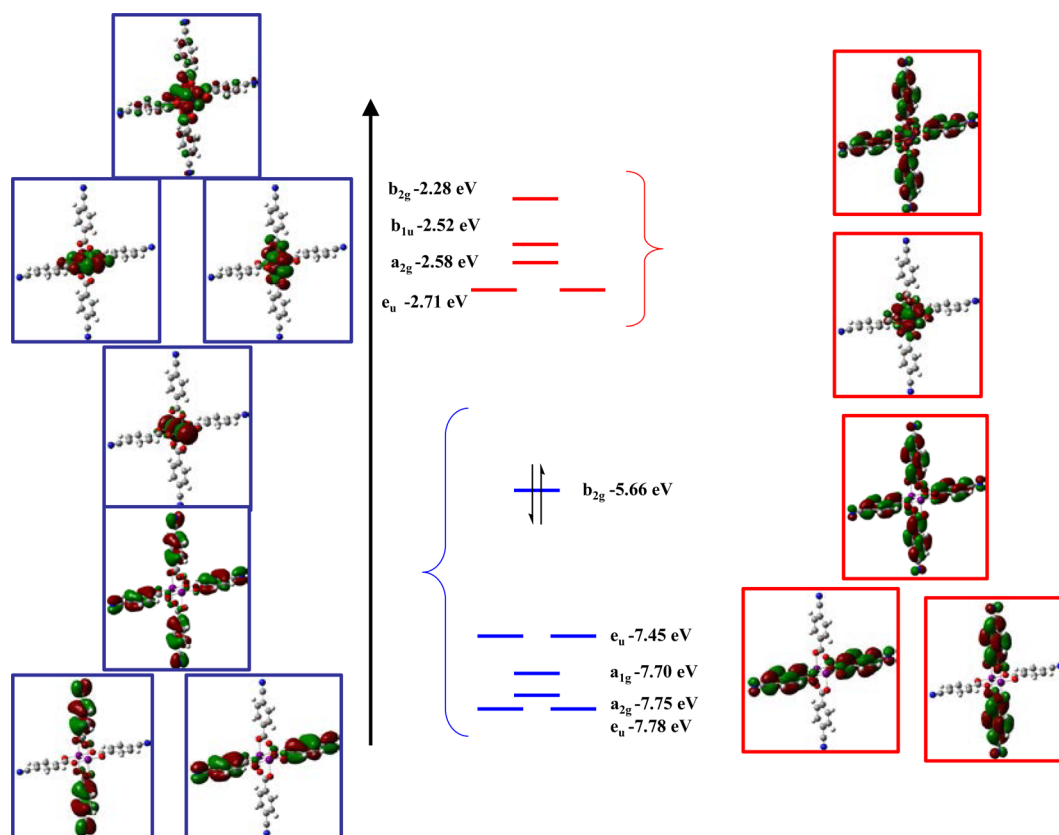
Figure 10. Frontier molecular orbital energy level diagram for the homoleptic $Mo_2(O_2CC_6H_4$-4-CN$)_4$ (adapted from ref 28).
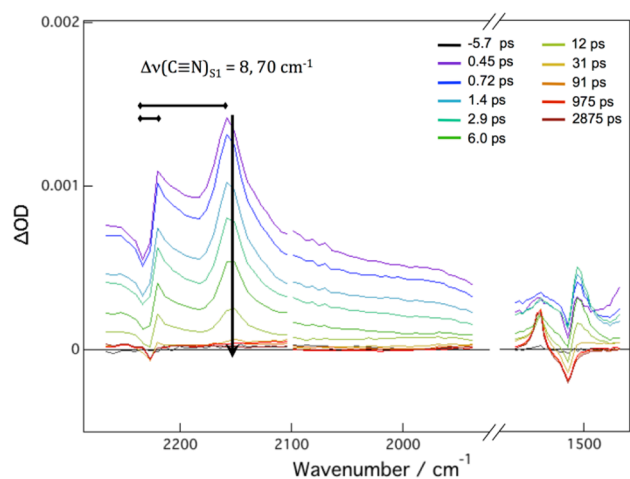

Figure 11. fs-TRIR spectra for the homoleptic $Mo_2(O_2CC_6H_5$-4-CN$)_4$, λ_{ex} = 515 nm (adapted from ref 28).
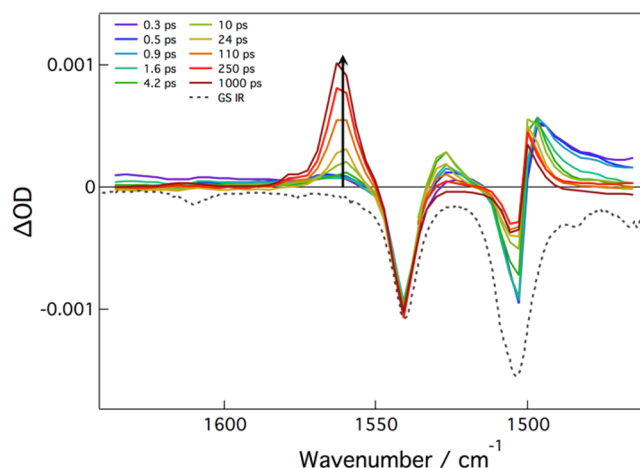
Figure 12. fs-TRIR spectra for the compound $Mo_2(DAnif)_3(O_2CBu^t)$ in THF at RT, λ_{ex} = 400 nm (adapted from ref 25).

quadruply bonded center. This allows for $M_2\delta$ to ligand π^*, MLCT transitions that can be tuned to span the region 400–1100 nm. Compared with the vast majority of transition metal complexes,[31−33] the [1]MLCT states have remarkably long lifetimes, typically 1–20 ps. The T_1 states may be either $^3MM\delta\delta^*$ or ^{3}MLCT. This has allowed the study of the S_1 and T_1 states by time-resolved spectroscopies and thus the examination of charge location and dynamics in the photoexcited states. Examples of charge localized and delocalized excited states representing excited state mixed valence of class I, II, and III behavior, respectively, have been observed by the employment of ligands incorporating C−X triple bonds whose

$\nu(C{\equiv}X)$ vibrations are sensitive to the degree of charge density in the C≡X π^* orbital in the photoexcited state. Although MLCT states have been the subject of extensive studies, few bear comparison with these quadruply bonded systems because ISC usually occurs within less than a picosecond. The alkynylplatinum(II) complexes of the form $trans$-Pt(PBu$^n_3$)$_2$(−C≡CAr)$_2$, for example, undergo rapid ISC[11] and in their T_1 $^3\pi\pi^*$/^{3}MLCT states show broken symmetry with the excited state electron localized on one ligand and some positive charge on the metal as evidenced by the appearance of two $\nu(C{\equiv}C)$ modes in the photoexcited state, one shifted ∼10 cm^{-1} to higher energy relative to the

ground state and the other to notably lower energy by ∼300 cm^{-1}.[22]

The current studies raise many fundamental questions such as why are the ^{1}MLCT states so long-lived, what determines whether a ^{1}MLCT state is delocalized or localized, and over what distance can charge be delocalized? Based on our current studies, we may speculate on the answers to these basic questions, but clearly more work needs to be done before reasonable hypotheses can be forwarded and experimentally tested.

It is also eminently apparent that the relatively long-lived photoexcited states and the absorptions that can be tuned to span the entire visible spectrum and move well into the near-infrared pose significant potential for photon-harvesting applications such as in photovoltaics and photocatalysis. Toward this end, we have already shown that these compounds can be employed for photoinduced charge transfer to electron acceptors such as perylene diimides[34] and the semiconducting oxide TiO$_2$.[35] Thus, even a half-century after their discovery, M$_2$ quadruply bonded units still afford some unique properties and avenues for new research.

■ AUTHOR INFORMATION

Corresponding Author

*Malcolm H. Chisholm. E-mail: chisholm@chemistry.ohio-state.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Malcolm Chisholm was born in Bombay, India, to Scottish parents and educated in England where he received his B.Sc. (1966) and Ph.D. (1969) from Queen Mary College London University under the direction of Professor D.C. Bradley, FRS. After postdoctoral studies with Professor H. C. Clark at the University of Western Ontario and faculty appointments at Princeton and Indiana Universities, he joined The Ohio State University in 2000 where he is currently a Distinguished University Professor. His research interests include transition metal and main group chemistry, catalysis, and materials chemistry. He is a member of the National Academies of Sciences in the U.S.A., U.K., and Germany and a Fellow of the American Academy of Arts and Science.

Samantha Brown-Xu received her B.A. in Chemistry and Integrated Science from Northwestern University in 2009. She was awarded an NSF Graduate Research Fellowship and an NDSEG fellowship and performed her graduate studies at The Ohio State University under the direction of Professors Malcolm Chisholm and Terry Gustafson. She obtained her Ph.D. in 2014 for work involving investigations of the photophysical and photosensitizing properties of dimetal complexes through ultrafast spectroscopy. Currently, Samantha has a postdoctoral appointment in the laboratory of Professor Lin Chen at Northwestern University and will be using time-resolved optical and X-ray techniques to study processes related to solar energy harvesting.

Thomas Spilker was born in Cleveland, Ohio, and received his B.S. (2009) in Chemistry from John Carroll University. He went on to complete his graduate studies at The Ohio State University with Professor Malcolm Chisholm. In 2014, he earned his Ph.D. with work

focusing on the formation of extended structures through post-synthetic modification of metallo-organic complexes and investigations of their photophysical properties. Currently, Thomas is pursuing postdoctoral studies at Case Western Reserve University with Professor Stuart Rowan, FRSC, working on stimuli responsive polymer materials.

■ ACKNOWLEDGMENTS

■ DEDICATION

On the occasion of the 50th anniversary of the recognition of the MM quadruple bond, this Account is dedicated to F. A. Cotton in memoriam.

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