Preparations and Photophysical Properties of Fused and Nonfused Thienyl Bridged MM (M = Mo or W) Quadruply Bonded Complexes

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A series of metal–metal quadruply bonded compounds [{(BuCO₂)_3M₂}µ-TT] where TT = thienothiophenedicarboxylate and M = Mo, 1A, and M = W, 1B and [{(BuCO₂)_3M₂}µ-DDT] where DDT = dithienothiophenedicarboxylate and M = Mo, 2A, and M = W, 2B, has been prepared and characterized by elemental analysis, ESI- and MALDI-TOF mass spectrometry and ¹H NMR spectroscopy. Their photophysical properties have also been investigated by steady-state absorption as well as transient absorption and emission spectroscopy. The optimized structures and the predicted low energy electronic transitions were obtained by DFT and time-dependent DFT calculations, respectively, on model compounds. These results, in combination with the respective properties of the compounds [{(BuCO₂)_3M₂}µ-BTh] (BTh = 2,5’-bithienyldicarboxylate, M = Mo, 3A, and M = W, 3B), allow us to make a comprehensive comparison of the fused (compounds 1A, 1B, 2A, and 2B) and the nonfused thienyl (compounds 3A and 3B) dicarboxylate bridged compounds of molybdenum and tungsten. The electrochemical studies show singly oxidized radical cations that are valence trapped on the EPR time-scale and are classified as Class 1 (M = Mo) or Class 2 (M = W) on the Robin and Day scale for mixed valence compounds. The new compounds exhibit intense metal to bridge charge transfer absorption bands in the far visible and near IR (NIR) region. Both molybdenum and tungsten complexes show dual emission, but for molybdenum, the phosphorescence is dominant while for tungsten the emission is primarily fluorescence. Femtosecond transient absorption spectroscopy shows that the relaxation dynamics of the S₁ states which have lifetimes of ~70 ps is dominated by intersystem crossing (ISC), leading to T₁ states that in turn possess long lifetimes, ~70 µs (M = Mo) or 3 µs (M = W). These properties are contrasted with the photophysical properties of conjugated organic systems incorporating metal ions of the later transition elements.

Introduction

Conjugated organic oligomers and polymers have attracted a great deal of interest over the past two decades due to their optoelectronic properties.¹⁻³ They represent a class of organic semiconductors that may be doped to become conducting and metallic-like.⁴⁻⁷ They also find applications in electronic devices such as organic field effect transistors (OFETs),⁸⁻⁹ organic light emitting diodes (OLEDs),¹⁰ polymer light

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emitting devices (PLEDs), photodiodes, photoswitches, etc., and several companies, including Cambridge Displays Technologies, Philips, and Seiko Epson, are pioneering their commercialization. Potential for commercialization arises from their synthetic flexibility, ease of processing by means of cheap technologies (spin-coating, ink-jet printing, and stamping) and the ability to change the physical properties of the polymer via the control of the molecular architecture. Among the several classes of conjugated organic polymers, the poly(2,5-thiophenes) and their derivatives are particularly well studied due to their low band gaps and good hole transport properties. Their properties are, however, greatly modified by the dihedral angles between the adjacent rings and the introduction of alkyl groups at the 3 and 4 positions, which leads to increased solubility of the polymers/oligomers and reduces the degree of aromatic conjugation, hence increasing the band gap. We have long been interested in the effect of incorporating MM quadruply bonded units (M = Mo or W) into oligothiophene structures by use of carboxylate linkers to effect M=O to thiophene conjugation. Three classes of compounds have been studied and their corresponding structures are depicted in Scheme 1.

Compounds of the type trans-\( \text{M}_2(\text{TiPB})_2(\mu-O_2C(\text{Th})_n)_2 \) (where \( n = 1, 2, \) and 3, TiPB = 2,4,6-tri-isopropylbenzoate, Th = thiényl) depicted as bis-bis and \( \text{(Bu}_4\text{N})_2\text{M}_2(\mu-O_2C(\text{Th})_n(3,4-n\text{-hexylTh})(\text{Th})_n\text{CO}_2)_2 \) depicted as dimers-of-dimers, in Scheme 1, can be viewed as a prototype for the polymers/oligomers \( \text{[M}_2(\text{TiPB})_2(\mu-O_2C(\text{Th})_n(3,4-n\text{-hexylTh})(\text{Th})_n\text{CO}_2)]_n \) where \( n = 1 \) or 2. The introduction of the 3,4-n-hexyl thienyl units greatly increases the solubility of the metallated polymers/oligomers thus allowing spin-coating of thin films for device applications. However, as noted before, they also cause a twisting and hence decrease the conjugation along a chain. In order to investigate and compare the properties of fused thienyl bridged complexes with those of nonfused thienyl bridged complexes, we decided to prepare some model compounds having fused thiophene rings. Herein, we describe the preparation and salient photophysical properties of MM quadruply bonded complexes linked by thienothiophenedicarboxylate, TT, dithienothiophenecarboxylate, DTT, and bithienyldicarboxylate ligands, BTh, shown in Figure 1. The DTT and BTh bridges place the dinuclear centers at an equivalent distance apart, \( \sim 15.00 \) (2A) and \( \sim 14.56 \) Å (3A), estimated from density functional theory calculations (vide infra) but differ with respect to the planarity of the bridge.

**Experimental Section**

**Measurements.** NMR spectra were recorded on a 400 MHz Bruker DPX Advance400 spectrometer. All \(^1\)H NMR chemical shifts are in ppm relative to the protio impurity in THF-d8 at 3.58 ppm or DMSO-d6 at 2.09 ppm.

Electronic spectra at room temperature were recorded using a Perkin-Elmer Lambda 900 spectrometer in THF solution. A 1.0 or 10.00 mm IR quartz cell was employed.

The cyclic voltammogram and differential pulse voltammogram of all the complexes were collected at a scan rate of 100 and 5 mV s\(^{-1}\) respectively, using a Princeton Applied Research (PAR) 173A potentiostat–galvanostat equipped with a PAR 176 current-to-voltage converter. Electrochemical measurements were performed under an inert atmosphere in a 0.5 M solution of \( \text{tBu}_4\text{NPF}_6 \) in THF inside a single compartment voltammetric cell equipped with a platinum working electrode, a platinum wire auxiliary electrode, and a pseudoreference electrode consisting of a silver wire in 0.5 M \( \text{tBu}_4\text{NPF}_6/\text{THF} \) separated from the bulk solution by a Vycor TM tip. The potential values are referenced to the FeCp2/FeCp2' couple, obtained by addition of a small amount of FeCp2 to the solution.
EPR measurements were made at the X-band (34 GHz) frequencies using a Bruker Elexys-500 spectrometer, equipped with an ER 051 GQ bridge.

Steady-state and nanosecond photophysical measurements were carried out in 10.0 × 10.0 mm² square quartz cuvettes equipped with Kontes stopcocks, while a 5.0 mm quartz tube was used in the 77 K steady-state NIR emission, and a 10.0 × 2.0 mm cell was used in the femtosecond approach. The absorption spectra were measured with a Hewlett-Packard diode array spectrophotometer (HP 8453), and the corrected steady-state luminescence spectra were recorded on a SPEX Fluoromax-2 spectrofluorimeter in UV–vis region. The steady-state NIR-luminescence spectra were measured on a home-built instrument excited at 514 (Ar⁺ laser) or 634 nm (He–Ne laser). The triplet emission lifetimes were also measured on the home-built instrument pumped by a frequency doubled (532 nm) or as an efficient optical parametric oscillator (OPO) crystal pumped by a Nd:YAG laser (700 nm, Continuum Surelite II Nd: YAG laser, fwhm ~8 ns, ~10 mJ per pulse), and the signal from the photomultiplier tube (Hamamatsu R928) was processed by a Tektronics 100 MHz oscilloscope (TDS 3012). Lifetime decays were fitted using OriginPro 7.0. To resolve the fluorescence at the end of which, red precipitate dropped out. This was filtered via a frit, washed with toluene (2 × 10 mL) and finally with hexane (10 mL) before being dried in vacuo to give 250 mg (70% yield) of a red solid. Microanalysis found: C 37.57, H 4.36, S 5.27%. C₃H₈O₂S₂Mo₂ requires: C 37.25, H 4.77, and S 5.55%. NMR (THF-d₈): δH (400 MHz) 8.05 (s, 2H), 1.41 (s, 18H), 1.38 (s, 36H) ppm. MALDI-TOF: calculated monoisotopic MW for C₃H₈O₂S₂Mo₂: 1216.73. found: 1217.9 (M⁺).

In the femtosecond transient absorption experiments, samples were excited at 420 (second harmonics) or 800 nm of a femtosecond Ti-sapphire oscillator (82 MHz, Spectra Physics) and monitored with a supercontinuum probe–pulse in the spectral range of 500–800 nm. The recorded spectra were time-corrected for the chirp of the supercontinuum. All transient signals were linearly dependent on the excitation power. The time resolution of the system is 300 fs, as determined by the two-photon absorption of methanol in the sample cell.

Microanalysis was performed by Atlantic Microlab Inc. (1A, 2A, and 3A) and H. Kolbe Microanalytisches Laboratorium (1B, 2B, and 3B).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) was performed on a Bruker Reflex III (Bruker, Breman, Germany) mass spectrometer operated in a linear, positive ion mode of oxygen-free UHP-grade argon using standard Schlenk line techniques in an atmosphere of oxygen-free UHP-grade argon and prepared with THF. THF dried over the appropriate drying agent was distilled prior to use and stored in reservoirs equipped with Kontes taps over activated 4 Å molecular sieves, under an argon atmosphere and degassed prior to use. The radical cations were generated in situ prior to EPR measurements, due to their instability, by treatment of all the neutral compounds with 0.75 equivalents of AgPF₆ in ether (1A, B, 2A, B) and THF (3A, B).

n-Butyllithium (2.5 M in hexanes) was purchased from Acros and used as received. All manipulations of the studied compounds were performed in a nitrogen-filled glovebox or by using standard Schlenk line techniques in an atmosphere of oxygen-free UHP-grade argon and prepared with THF. THF dried over the appropriate drying agent was distilled prior to use and stored in reservoirs equipped with Kontes taps over activated 4 Å molecular sieves, under an argon atmosphere and degassed prior to use. The radical cations were generated in situ prior to EPR measurements, due to their instability, by treatment of all the neutral compounds with 0.75 equivalents of AgPF₆ in ether (1A, B, 2A, B) and THF (3A, B).
MALDI-TOF: calculated monoisotopic MW for C₉₀H₇₀O₆₆S₂Mo₄, 1242.77, found 1243.5 (M+).

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[\{\text{[BuCO}_2\text{O}_3\text{W}_2]\text{[\mu-BTh]}\}] \text{(3B)}
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The reaction was performed under similar conditions to those described for the preparation of 1B, by using 0.4120 g of W₂(O₂CBu)₄ (0.534 mmol) and 0.0690 g of BTh (0.267 mmol). A blue solid (220 mg, 52% yield) was isolated after 7 days of stirring at room temperature. Microanalysis found: C 30.58, H 3.78%. C₄₀H₅₈O₁₆S₂W₄ requires: C 30.13, H 3.67%. NMR (THF-\(d_8\)): \(\delta\) H (400 MHz) 7.31 (d, 2H, \(J = 4 \text{ Hz}\)), 7.20 (d, 2H, \(J_{HH} = 4 \text{ Hz}\)), 1.43 (s, 18H), 1.40 (s, 36H) ppm.

Theoretical Approaches. Electronic structure calculations on the model compounds of the type \([\{\text{HCO}_2\text{O}_3\text{M}_2\}\text{[\mu-X]}\] where X = TT, DTT, and BTh and M = Mo and W were performed using density functional theory (DFT)\(^{26–29}\) with the aid of the Gaussian03 suite of programs.\(^{30–36}\) The B3LYP\(^{31,32}\) exchange correlation functional was used along with the 6-31G* basis set for C, H, and O, 6-31+G (2d) basis set for S, and the SDD energy consistent pseudopotentials for molybdenum and tungsten. Geometry optimizations were performed in appropriate symmetry and were confirmed as local minima on the potential energy surfaces using frequency analysis. Pivitate groups were substituted by formate groups to reduce calculation time. Orbital analyses were preformed using Gaussview.\(^{33}\) Time-dependent density functional theory was employed to predict optical transition spectra for the model complexes using same basis sets.\(^{34–36}\) Calculations were also performed for the lowest energy triplet excited-state T1, using the unrestricted B3LYP (UB3LYP) exchange correlation functional and the same basis sets.

Results and Discussion

Syntheses. The series of new compounds were synthesized from the reactions between the M₂(O₂CBu)₄ precursors and the respective dicarboxylic acids as shown in Scheme 2. The pale yellow toluene solutions of M₂(O₂CBu)₄ rapidly darkened as the reactions proceeded and the new compounds were formed as fine powders, being only very sparingly soluble in toluene. The molybdenum complexes \([\{\text{BuCO}_2\text{O}_3\text{Mo}_2\}\text{[\mu-TT]}\], 1A, and \([\{\text{BuCO}_2\text{O}_3\text{Mo}_2\}\text{[\mu-DTT]}\], 2A, were bright orange or red while their respective tungsten analogues 1B and 2B were blue. All the compounds were air-sensitive and soluble in THF and other donor solvents such as DMSO. They showed molecular ions by MALDI-TOF mass spectrometry and their \(^1\text{H}\) NMR spectra were consistent with expectations.

Electrochemical Studies. The prepared compounds have been examined by cyclic voltammetry and differential pulse voltammetry. All of the molybdenum containing compounds show a single reversible or quasi-reversible oxidation close to the Cp₂Fe⁰/¹⁺ couple in THF solutions with \(\text{Bu}_4\text{NPF}_6\) as counter electrolyte. The tungsten complexes, in contrast, are notably easier to oxidize and show two reversible or quasi-reversible oxidations as shown in Figure 2. In each instance, we assign these oxidations as being M₂β₂ corresponding to removal of an electron from an M₂β orbital and this is supported by both the EPR spectra and the predictions of electronic structure based on DFT calculations (vide infra).

\[\text{Scheme 2. Illustration of the synthetic aim in this study}\]

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![Diagram](image.png)

**Figure 2.** Differential pulse voltammogram (DPV) for \([\{\text{BuCO}_2\text{O}_3\text{Mo}_2\}\text{[\mu-TT]}\] (red) and \([\{\text{BuCO}_2\text{O}_3\text{W}_2\}\text{[\mu-DTT]}\] (blue) in a 0.1 M \(\text{Bu}_4\text{NPF}_6\)/THF solution. Potentials are referenced to the FeCP₂⁰⁺/¹⁺ couple.
The presence of a single oxidation wave corresponding to the removal of two electrons for the molybdenum complexes is a clear indication of valence trapped behavior and the property of a Class I mixed valence compound on the Robin and Day classification scheme.\textsuperscript{37} For the tungsten compounds the separation between the first and second oxidation potentials follows the order 1B (182) \textgreater 2B (108) \textgreater 3B (90 mV), indicative of the influence of both W\textsubscript{2} to W\textsubscript{2} distance, 1B (12.93) \textless 2B (13.76) \textless 3B (14.55 Å), and the greater coupling within the fused ring compounds. In the Robin and Day scheme, these compounds can reasonably be assigned as Class II. In contrast, the complex \([\text{Bu} \text{CO}_2]_2\)\([\mu-2,5-\text{Th(CO}_2)_3]_2\) containing a single thiényl ring, which brings the \(W_2\) to W\textsubscript{2} distance to 10 Å, shows two oxidation waves separated by 310 mV, and the singly oxidized radical cation has been assigned as fully delocalized or Class III in the Robin and Day scheme based on UV–vis NIR and EPR data.\textsuperscript{18}

**EPR Studies.** Supplementary support of the previous assignment is given by the EPR spectra. Oxidation of the neutral compounds with 0.75 equiv of AgPF\textsubscript{6} yields radical cations that are kinetically labile and decompose within hours at room temperature. Nevertheless, these radical cations are sufficiently persistent for studies by EPR spectroscopy in diethyl ether and THF at \(-50^\circ\text{C}\). The molybdenum complex 1A\textsuperscript{+} showed an isotropic spectrum at \(-50^\circ\text{C}\) consisting of a central resonance at \(g \sim 1.94\) flanked by a satellite spectrum of 6 lines due to the hyperfine coupling with \(^{95/97}\text{Mo}\) nuclei that have \(I = \frac{1}{2}\), a similar magnetic moment, and a combined natural abundance of \(\sim 25\%\). The magnitude of the hyperfine coupling, \(A_0\), was \(\sim 27\) G which is typical for a Mo(II)\textsubscript{2}(O\textsubscript{2}C\textsubscript{2})\textsubscript{4}\textsuperscript{+} cation and together with the integral intensities of the hyperfine spectrum was indicative of a valence trapped radical. Under similar conditions, the tungsten complex ion 1B\textsuperscript{+} showed an isotropic spectrum consisting of a central signal, \(g \sim 1.81\), flanked by satellites due to coupling to \(^{183}\text{W}\), \(I = \frac{3}{2}\), 14.5% natural abundance. The magnitude of the hyperfine coupling to \(^{183}\text{W}\), \(A_0\), was 53 G, typical of a W\textsubscript{2}(O\textsubscript{2}C\textsubscript{2})\textsubscript{4}\textsuperscript{+} ion which taken together with the relative intensities of the hyperfine spectrum once again indicated the valence trapped nature of the unpaired electron on the EPR time scale. In contrast, the spectrum of the radical cation of \([\text{Bu} \text{CO}_2]_2\)\([\mu-2,5-\text{Th(CO}_2)_3]_2\) formed upon oxidation with AgPF\textsubscript{6} showed evidence for complete delocalization of the unpaired electron over all four W atoms with \(A_0 \sim 29\) G, \(g = 1.83\).\textsuperscript{18}

**Electronic Absorption Spectra.** The absorption spectra of molybdenum compounds 1A and 2A are shown in Figure 3, along with that of the bithienylidicarboxylate bridged compound \([\text{Bu} \text{CO}_2]_2\)Mo\textsubscript{2}(\(\mu-B\text{Th})_2\), 3A. All the compounds show an intense \(S_0 \rightarrow S_1\) absorption band at around 530 nm that gives rise to their purple color in THF. This band originates from a metal-to-bridge ligand charge transfer (MLCT) mixed with some intraligand \(\pi-\pi^*\) transition (LLCT) in character as anticipated by the nature of the HOMO and LUMO (Figure 10, vide infra). We anticipate

the tungsten compounds where the $S_0 \rightarrow S_1$ transition is dominated by $M_2\delta \rightarrow \text{bridge-} \pi^*$, the spectral shift may not be obvious due to the smaller contribution from the thiophene ligand $\pi - \pi^*$ transition. We also note that for the same number of the thiophene rings, the nonfused compound 3A (or 3B) tends to have more diffusive spectral profile and red-shifted spectral onset region with respect to the fused compound 1A (or 1B) and 2A (or 2B), manifesting more rotational degrees of freedom for the nonfused 3A (or 3B) in the room temperature THF solution.

**Luminescence.** All the titled compounds exhibit far visible to near-infrared (NIR) emission in the region of 700–1400 nm, and a comparison of the emission spectra for the thienothiophenedicarboxylate bridged compounds 1A versus 1B is shown in Figure 5. In the steady-state measurement, 1A emits primarily at 800 nm with a peak wavelength at $\sim$1100 nm. In comparison to the absorption maximum at $\sim$520 nm, it is very unlikely that the emission originates from the fluorescence. Time-resolved measurements further resolved a single decay component with a lifetime as long as $\sim$70 $\mu$s for the 1100 nm emission in the N$_2$ filled THF (1 atm, see the Experimental Section), confirming its assignment to a spin-forbidden transition, namely the phosphorescence. To resolve the presumably very weak and obscure fluorescence in 1A, we further performed an experiment, in which the electronic gate of the intensified charge coupled detector (ICCD) was activated at within 10 ns after the excitation pulse to eliminate the phosphorescence interference. We then acquired the fluorescence with a peak wavelength at 710 nm for 1A (see Figure 5). For the tungsten compound 1B, the assignment of the 970 nm emission band to a fluorescence seems to be unambiguous owing to its rather short decay time ($<10$ ns, vide infra) and well-correlated mirror image with respect to the $S_0 \rightarrow S_1$ absorption band. Nevertheless, an obvious shoulder extending from 1200 to 1400 nm cannot be neglected. Upon monitoring at 1300 nm, in addition to a system response limited decay ($<10$ ns) that is attributed to the residue of the fluorescence, the NIR time-resolved measurement (see the Experimental Section) resolved a much longer decay component with a lifetime of 3.5 $\mu$s. Accordingly, this $\sim$1300 nm emission band is reasonably assigned to a phosphorescence of 1B.

Using the same methods as above, i.e. the steady-state NIR measurement coupled with the pulse-laser coupled ICCD time-resolved experiment, dual emission was clearly resolved for all the molybdenum compounds, consisting of a structureless fluorescence band maximized at 700–730 nm and a vibronically progressing phosphorescence band with the first peak wavelength at $\sim$950 nm. The fluorescence peak wavelength of 2A ($\sim$705) > 1A ($\sim$690 nm) is consistent with the trend observed in the $S_0 - S_1$ absorption. However, despite the same absorption peak of $\sim$520 nm for 1A and 3A, the Stokes shift (peak-to-peak between absorption and emission) for the nonfused thienyl compound 3A ($\lambda_{em} \sim$720 nm) is notably larger, as seen in Figure 6, manifesting its more significant change in geometry (toward the planar configuration) in the excited state. Monitored by the time-resolved NIR, the fluorescence decay was system response limited ($<10$ ns) for 1A, 2A, and 3A, most probably indicating a fast rate of intersystem crossing assuming that other radiationless decay channels play minor roles. Detailed singlet excited-state relaxation dynamics will be elaborated in the section dealing with femtosecond transient absorption spectra, vide infra.

A comparison of the phosphorescence among molybdenum complexes 1A, 2A, and 3A is depicted in Figure 6. Given the limitations of the NIR detector in the range 600–900 nm, we are not able to comment on the features seen in the spectra within this range except for the spectra shown in the insert which were obtained using an ICCD which itself is limited in the range 800–900 nm. The notion that we might be observing vibronic features can be dismissed on the basis that the apparent peak separation for compounds 3A (green) and 2A (red) is $>1600$ cm$^{-1}$ which is not compatible with a symmetric stretching mode of the bridging thienyl dicarboxylate. The $S_1 - T_1$ energy gap, which is taken by subtract-

**Figure 5.** Emission spectra of 1A = [([BuCO$_2$]$_3$Mo$_2$)(µ-TT) (red), (F)$_1\alpha$ fluorescence, P$_{1\alpha}$ phosphorescence) and 1B = ([BuCO$_2$]$_3$W$_2$(µ-TT) (blue), (F$_{1\alpha}$ fluorescence, P$_{1\beta}$ phosphorescence) in N$_2$ filled (1 atm) THF at room temperature. The excitation wavelength is the S$_0$–S$_1$ absorption peak wavelength (see Figures 2 and 3). Note that the fluorescence of ([BuCO$_2$]$_3$Mo$_2$)(µ-TT) was acquired from a time-gated (10 ns) intensified charge coupled detector (see text).

**Figure 6.** Phosphorescence spectra of [([BuCO$_2$]$_3$Mo$_2$)(µ-TT) (black), ([BuCO$_2$]$_3$Mo$_2$)(µ-DTT) (red), and ([BuCO$_2$]$_3$Mo$_2$)(µ-BTh) (green). (inset) Corresponding fluorescence spectra. All measurements were performed in N$_2$ (1 atm) filled THF at room temperature. The term $\lambda_{em}$ is the absorption peak wavelength.
was excited at the lowest lying transition of 770 nm and the S\textsubscript{1} level, i.e. the S\textsubscript{1} relaxation dynamics, was resolved for both compounds in the detecting range of 0.4 ps (Figure 5), the room temperature fluorescence and phosphorescence were not well resolvable in 2B and 3B. Nevertheless, as shown in Figure 7, all tungsten compounds exhibit a distinct fluorescence band maximized at 970–1000 nm, accompanied by a shoulder around 1300 nm. The phosphorescence was further resolved to reveal a peak wavelength at \( \sim 1250 \) nm in the 77 K THF matrix (see insert of Figure 7). Among the tungsten compounds, 3B exhibits the longest fluorescence peak wavelength at \( \sim 1000 \) nm, the result of which is consistent with a trend observed in the S\textsubscript{0} – S\textsubscript{1} absorption (vide supra). Further estimation rendered an S\textsubscript{1} – T\textsubscript{1} energy gap of \(< 7.0 \) kcal mol\(^{-1}\) for all tungsten compounds, which is notably smaller than those observed for the molybdenum compounds.

**Transient Absorption Spectroscopy.** To gain further insight into the excited-state relaxation dynamics, femtosecond transient absorption measurements were performed for each compound. As a prototypical illustration, the resulting temporal evolution of the transient absorption for 2A and 2B and their corresponding rise and decay traces are depicted in Figures 8 and 9, respectively.

As shown in Figures 8 and 9, 2A and 2B reveal distinct transient absorption bands maximized at 650 and 520 nm, respectively. The corresponding relaxation dynamics for both 2A and 2B can be well-described by a system response-limited rise (\( \sim 350 \) fs), followed by a picosecond decay component, which was fitted to be 11.5 ± 0.4 (2A) and 12 ± 0.4 ps (2B) in THF. Finally, a nonzero constant component was resolved for both compounds in the detecting range of 50 ps. Note that the Franck–Condon excitation wavelength to prepare Figures 8 and 9 is 420 nm, which is well above the S\textsubscript{1} level, i.e. the S\textsubscript{n} \( (n > 1) \) with a LLCT (\( \pi-\pi^* \)) character. Therefore, the S\textsubscript{n} – S\textsubscript{1} relaxation dynamics, namely the internal conversion, has to be considered. For 2B, an additional experiment was performed in which 2B was excited at the lowest lying transition of 770 nm and the resulting traces monitored at 650 nm.

**Emission Spectra.** The observed longest fluorescence peak \( \sim 1250 \) nm in the 77 K THF matrix (see insert of Figure 7) was due to the stray light. (insert) Corresponding emission spectra measured in the 77 K THF matrix. Note that the increase of \( \Delta T \) transition.38

\[ \text{Emission spectra (fluorescence and phosphorescence)} \]

\[ \text{of [(BuCO\textsubscript{3})\textsubscript{2}W\textsubscript{2}(µ-CT)] (black), [(BuCO\textsubscript{3})\textsubscript{2}W\textsubscript{2}(µ-DTT)] (red), and [(BuCO\textsubscript{3})\textsubscript{2}W\textsubscript{2}(µ-BTh)] (green) measured in N\textsubscript{2} (1 atm) filled THF at room temperature.} \]

\[ \text{Corresponding rise and decay traces monitored at 650 nm.} \]

\[ \text{Corresponding emission spectra measured in the 77 K THF matrix.} \]

\[ \text{Note that the increase of \( \Delta T \) transition.38} \]

**Continuous Observation.** Inorganic Chemistry, Vol. 47, No. 8, 2008 3421
intriguing. It is possible the introduction of the carboxylate linker induces an adverse spin–orbit coupling between the M2 and thienyl centers. Alternatively, the correlation between ISC rate and effective spin–orbit coupling distance may serve as another key factor. As a simplified approach based on the hydrogen-like atom, the rate of intersystem crossing is inversely proportional to $r^{6.40}$ Although an analogous correlation can never be used for complicated molecules like the titled compounds, we can make a qualitative comparison. For example, monitored by the femtosecond transient absorption, the rate of intersystem crossing of $1A \rightarrow 2A$ (12 ps) can be rationalized by the increasing numbers of the fused thiophene moiety, hence lengthening the effective distance $r$ between the metal center and the thiophene moiety. For both the multinuclear Mo and W complexes examined in this study, the metal centered HOMO and thiophene based LUMO are bridged by a carboxylate functional group. This increase in separation is expected to reduce the rate of ISC and recently, the effect of distance tuning the ISC rate has been reported in several third-row transition metal complexes.$^{41–43}$

It is also worthy of note that the long metal–ligand effective distance reduces the spin–orbit coupling and hence leads to the reduction of the $S_1 \rightarrow T_1$ state mixing. Accord -ingly, due to the reduced singlet-manifold contribution in $T_1$, the corresponding $T_1 \rightarrow S_0$ transition is expected to be less favorable, resulting in a long radiative lifetime. This viewpoint is apparently applicable for the studied complexes. Taking the phosphorescence quantum yield, $\Phi_p$, generally observed to be $<0.01$, the radiative lifetime $\tau_r$, calculated via $\tau_r = \frac{\tau_{obs}/\Phi_p}{\tau_{obs}}$, was deduced to be several to tens of milliseconds for all complexes studied. Such a long radiative lifetime is in sharp contrast to most Ir, Os, and Pt mononuclear complexes applied in OLEDs, for which a short radiative lifetime of e.g. $<10 \mu s$ is required to avoid any defect trapping prior to the charge recombination.$^{39}$

Electronic Structure Calculations. To gain a more quantitative understanding of the bonding in these complexes, electronic structure calculations were performed using density functional theory (DFT). The computations were carried out using the Vienna Ab initio Simulation Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional$^{44}$ and the projector augmented wave (PAW) method.$^{45}$ The k-point mesh for the Monkhorst-Pack scheme was chosen to be 2x2x1 for all calculations. The cutoff energy for the plane wave basis was set to 450 eV. The convergence criteria for the total energy and force per atom were set to $10^{-5}$ eV/atom and $10^{-2}$ eV/Å, respectively. The electronic structures of the title compounds were calculated using the same set of parameters.

Table 1. Photophysical Data of Molybdenum and Tungsten Compounds in THF at Room Temperature$^a$

| compounds | $\lambda_{abs}$, nm ($\epsilon \times 10^{-3}$) & $\lambda_{em}$, nm | $\lambda_{trans}$, nm | $\tau (S_1)$, ps ± 0.02 | $\tau (T_1)$, $\mu$s |
|-----------|---------------------------------|----------------|-----------------|----------------|----------------|
| $[(t\text{BuCO}_2)_3\text{Mo}_2](\mu-\text{TT})$ | 525 (57.434) | 690 | 655 | 7.9 | 69 ± 2.1 |
| $[(t\text{BuCO}_2)_3\text{Mo}_2](\mu-DTT)$ | 534 (48.400) | 700 | 633 | 11 | 60 ± 2.1 |
| $[(t\text{BuCO}_2)_3\text{Mo}_2](\mu-BTh)$ | 520 (53.358) | 720 | 620 | 8.6 | 72 ± 2.1 |
| $[(t\text{BuCO}_2)_3\text{W}_2](\mu-\text{TT})$ | 790 (209.000) | 960 | 633 | 11 | 60 ± 2.1 |
| $[(t\text{BuCO}_2)_3\text{W}_2](\mu-DTT)$ | 795 (61.714) | 965 | 525 | 12 | 2.8 ± 0.1 |
| $[(t\text{BuCO}_2)_3\text{W}_2](\mu-BTh)$ | 790 (75.776) | 980 | 526 | 14 | 3.6 ± 0.1 |

$^a$ All experiments were performed in the N$_2$ (1 atm) filled THF solution. $^b$ The peak wavelength of the transient absorption. $^c$ Not observed due to sample decomposition.


pounds, we undertook electronic structure calculations employing density functional theory. In this approach the bulky pivalate ligands are replaced by formate groups to simplify the computational time. Such a truncation has been found to be useful in examining the electronic structures of bridged compounds of the form \([\text{HC}O_2\text{M}_2\text{X}_2\mu\text{-TT}]\) where \(M = \text{Mo or W and X} = \text{oxalate, perfluoroterephthalate and related aryl dicarboxylates, thiophene, 2,5-thienyldicarboxylate, and 2,6-azulenedicarboxylate.}\) The compounds 1(A,B) were geometry optimized in \(C_{2h}\) symmetry while 2(A,B) and 3(A,B) were optimized in \(C_3\) and \(C_1\) geometry, respectively. In the geometry optimized ground-state structures for 1(A,B) and 2(A,B), it was found that the fused thiophene rings are planar with respect to the \(M_2\) centers. This facilitates extended \(\pi\) delocalization and introduces greater \(M \& \pi\)–bridge \(\pi\) electronic coupling in these systems.

For the model compounds of 3A and 3B, however, the rings of the thiophene were found to be twisted by an angle of 148° resulting in a loss of planarity with the \(M_2\) centers. This alludes to the fact that facile electron delocalization across the \(M_2\) centers via the BTh bridge is hindered resulting in a lesser degree of electronic communication in these compounds.

The frontier molecular orbitals were plotted in Gaussview with isosurface value of 0.02, and it was found that, for all the compounds, the HOMO and HOMO – 1 were combinations of the \(M_2\) \(\sigma\) and ligand \(\pi\) orbitals. The LUMO in each case was a thiophene based \(\pi^*\) orbital. Time-dependent DFT calculations showed that the lowest energy transition primarily involved HOMO to LUMO transition as was verified experimentally from the absorption maxima and the high value of the extinction coefficient (Table 2).

The \(S_0 \rightarrow S_1\) energy gap for the calculated model compounds pertain to the model formate compounds in the gas phase while the experimental data pertain to pivalate complexes in THF. In spite of that, the close correlation between calculated and experimental values for the model compound of 1A is highly encouraging. The much larger discrepancy between the predictions and the observed data for the tungsten complexes has been seen before in calculations pertaining to bridged dicarboxylate compounds and presumably arises, at least in part, due to greater spin–orbit coupling associated with the heavy third row transition element.

Figure 10 shows a comparison of the energy levels of the frontier molecular orbitals (FMOs) of the model compounds pertaining to 1A and 1B along with the Gaussview plots of selected FMO’s of 1A. Some of the salient features observed in this figure are described below.

The calculated HOMO and HOMO – 1 for the tungsten complex are relatively higher in energy than those of the molybdenum, while the LUMO which is primarily thiophene \(\pi^*\) based remain essentially unchanged in energy. This observation is consistent with the results from cyclic voltammetry. Also the absorption spectra reveal the lower energy of the HOMO–LUMO transition for the tungsten complexes (vide supra) which points to the easier oxidation of the tungsten complexes. It is also worthy of mention that the calculations indicate that in all cases the LUMO is not an \(M_2\) \(\delta^*\) combination and furthermore that the ordering of the bridge based filled \(\pi\) orbitals of highest energy (depicted in Figure 10) lie below the \(M_2\) \(\delta\) combinations and above the \(M_2\) \(\sigma^*\)’s. For tungsten, these filled thienyl \(\pi\)–orbitals fall between the \(W_2\) \(\pi\) and \(W_2\) \(\sigma\) combinations.

When comparing the various bridges, TT, DTT, and BTH, it was found that model compounds of 2(A,B) showed the lowest energy gap between HOMO and LUMO while TT and BTH showed nearly similar gaps as seen in Figure 11. This is explained from the fact that DTT bridging ligand has three thiophene rings which are fused together and confined in the same plane as the \(M_2\) centers. This results in the lowering of the thiophene \(\pi^*\) orbitals and consequently reduces the energy gap. The lower number of fused rings in 1(A,B) and the twisting of the thienyl rings in 3(A,B) results in larger energy gap. This trend is observed in the lower oxidation potential of 2(A,B) compared to 1(A,B) which in turn is lower than 3(A,B) [see the Supporting Information]. Furthermore, 2(A,B) show the greatest red-shift in the absorption maxima of their lowest energy electronic transition, while a higher energy MLCT transition is seen for 1(A,B) and the highest for 3(A,B).

Calculations were also performed on the lowest energy triplet state, \(T_1\), of the model compounds. In all cases the geometries of the model formate complexes for 1A, 1B, 2A, 2B, 3A, and 3B were optimized and the frequency analysis

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**Table 2.** Comparison of Lowest Energy Transition (HOMO → LUMO) Calculated by TD-DFT for Model Compounds \([\text{HC}O_2\text{M}_2\text{X}_2\mu\text{-TT}]\) and \([\text{HCO}_2\text{W}_2\mu\text{-TT}]\) with the Experimentally Observed MLCT Band for \([\text{BuCO}_2\text{M}_2\text{X}_2\mu\text{-TT}]\) and \([\text{BuCO}_2\text{W}_2\mu\text{-TT}]\) (μ-TT).

<table>
<thead>
<tr>
<th>(\lambda_{calc}) (nm)</th>
<th>(\Delta E_{calc}) (eV)</th>
<th>(f_{osc})</th>
<th>(\lambda_{obs}) (nm)</th>
<th>(\Delta E_{obs}) (eV)</th>
<th>(\epsilon) (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{BuCO}_2\text{Mo}_2\mu\text{-TT}])</td>
<td>519</td>
<td>2.39</td>
<td>521</td>
<td>2.38</td>
<td>~60 000</td>
</tr>
<tr>
<td>([\text{BuCO}_2\text{W}_2\mu\text{-TT}])</td>
<td>619</td>
<td>2.66</td>
<td>715</td>
<td>1.73</td>
<td>~200 000</td>
</tr>
</tbody>
</table>

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revealed that these were local minima on the potential energy surface. We have not done time dependent DFT calculations to attempt to correlate the energies of the emissive triplet states but rather have used these calculations to examine the formal nature of the states. For the molybdenum complexes 1A and 3A, the calculations suggest that the T$_1$ state is best described as a $^3$MM($\delta\delta^*$) state and the tungsten complex 3B is similarly described. For the molybdenum complex 2A, having three fused rings and for the tungsten complexes 1B and 2B, the T$_1$ state is $^3$MLCT involving a metal $\delta$ combination and the bridge $\pi^*$. The difference between the molybdenum and tungsten complexes primarily owes its origin in the relative positioning of the M$_2\delta$ and $\delta^*$ manifolds. The relative energy of the bridge based $\pi^*$ orbitals is primarily determined by the degree of conjugation which brings DTT (three fused rings) bridge to a lower energy than the others. For the bithiophene bridge, the dihedral angle between the two thiophene rings decreases the conjugation. A comparison of the calculated $^3$MM($\delta\delta^*$) and $^3$MLCT states for the model compounds for 1A and 1B are represented by the Gaussview plots shown in Figure 12. Related Gaussview plots for the T$_1$ states of the model compounds for 2A, 2B, 3A, and 3B are shown in the Supporting Information.

Concluding Remarks

In conclusion, a new series of fused thienyl dicarboxylate bridged MM (M = Mo or W) quadruply bonded complexes has been prepared and associated electrochemical and photophysical properties investigated and compared with the previously reported nonfused thienyl complex.$^{18}$ On the basis of steady-state absorption/emission NIR time-resolved dynamics and femtosecond transient absorption studies, the associated photophysical properties can be generalized and depicted by using the simplified Jablonski diagram shown in Figure 13. Upon $^1$LLCT excitation ultrafast ($<350$ fs) $S_0$ ($^1$LLCT) $\rightarrow S_1$ ($^1$MLCT/$\pi\pi^*$) internal conversion takes place, followed by a relatively slow ($\sim$ few to tens of picoseconds) $S_1$ ($^1$MLCT/$\pi\pi^*$) $\rightarrow$ T$_1$ intersystem crossing, giving rise to dual emission, i.e. fluorescence and phosphorescence. The lifetimes of phosphorescence were resolved to be within a few to tens of microseconds for all titled compounds. The calculations on the model compounds suggest that the nature of the T$_1$ states is dependent on both the metal and the bridge. This is clearly a very interesting suggestion and warrants further experimental work. We plan further studies involving time-resolved Raman and infrared spectroscopies to address these issues.

The majority of the work previously reported for metal-lated thiophene systems has involved the more electronegative late transition elements such as Au,$^{48}$ Pt,$^{49}$ Ru,$^{50}$ and Os.$^{51}$ In most of these systems, the lowest energy absorptions arise for $^1$LLCT with some metal d orbital mixing because the highest occupied metal orbitals lie below those of the ligand. This is not the case for Ru (II) and Os (II) where the...
first oxidation is metal based and the lowest energy absorp-
tion is 1MLCT.\textsuperscript{50,51} However, this is very close in energy to
LLCT and occurs at wavelength in the region 400–500 nm
and the change in going from Ru to Os produces a very
modest red shift. In our studies, we see much lower energy
absorptions arising from 1MLCT due to the higher energy
of the M$_2$ $\delta$ orbitals. Furthermore, we observe a very signi-
ficant red shift of 0.65 eV in going from the second row
metal Mo to the third row metal W. Thus, the M$_2$ metallated
thienyl carboxylates of molybdenum and tungsten having
quadruple bonds may find applications in solar energy
conversion due to their intense absorptions which span the
region 300–800 nm (see Figures 3 and 4 and the Supporting
Information) and their long-lived photoexcited states. Also,
we note that in the systems reported here we observed both
phosphorescence and fluorescence at room temperature. This
is also quite unusual when compared to the metallated oligothio-
phenes of the later transition elements.\textsuperscript{52} Given the growing
interest in NIR emitters,\textsuperscript{53–55} with potential applications for
night vision displays and sensors, we plan further studies
on related systems.

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help with computational calculations.

**Supporting Information Available:** Listings of electrochemical
data and computational calculations of triplet states of Mo and W
complexes. This material is available free of charge via the Internet
at http://pubs.acs.org.

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