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# Introduction

There is considerable current interest in the synthesis of molecular systems that enhance spectral absorption across the solar spectrum for photon harvesting and application to photovoltaics, PV.1 Both organic and metalloorganic compounds are under consideration in various forms of dye sensitized solar cell (DSSC) devices. Numerous push-pull molecules with a donor-acceptor (D-A) or donor- $\pi$ bridge acceptor (D– $\pi$ –A) architecture are being intensely studied for application in optoelectronic devices such as solar cells; since it is possible to tune the photophysical and structural properties of these systems through the nature and arrangement of D and A moieties.2-6 These push-pull molecules have been employed to enhance spectral expansion to cover more of the sun's radiation.7 Representative examples of some of the organic and metalloorganic compounds are shown in Chart 1.7-10 The Ru(II)bipyridine-based dyes have been largely employed in Grätzel type solar cells7,11 while platinum based polymers and organic oligomers are employed in thin film polymer or bulk heterojunction PV cells.8-10

We are currently evaluating the photophysical properties of carboxylate supported MM quadruply bonded complexes and their oligomers with regard to photon harvesting and their potential in PV devices. These complexes show intense metal to

# MM quadruple bonds supported by cyanoacrylate ligands. Extending photon harvesting into the near infrared and studies of the MLCT states†

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The compounds  $trans-M_2(T^iPB)_2(L)_2$  and  $trans-M_2(T^iPB)_2(L')_2$  have been prepared from the reactions between  $M_2(T^iPB)_4$  ( $T^iPB = 2,4,6$ -triisopropylbenzoate, M = Mo or W) and LH or L'H (~2 equiv.), respectively, where  $L = O_2CC(CN)=CH-C_6H_4$ -NPh<sub>2</sub> and  $L' = O_2CC(CN)=CH-C_4H_3S-C_6H_4$ -NPh<sub>2</sub>. These cyanoacrylate ligands promote intense  $M_2\delta$  to L or L'  $\pi^*$ -transitions that span the range 550–1100 nm. The two molybdenum complexes have been characterized by single crystal X-ray studies that reveal the extensive  $L-M_2-L$  or  $L'-M_2-L'$   $M_2\delta$ -ligand  $\pi$ -conjugation. The new compounds have been characterized by electronic structure calculations employing density functional theory (DFT) and time-dependent-DFT, cyclic voltammetry, electronic absorption and steady state emission spectroscopy and femtosecond (fs) and nanosecond (ns) time resolved transient absorption (TA) and fs time-resolved infrared spectroscopy (TRIR). The latter allows the determination of the S<sub>1</sub> states as <sup>1</sup>MLCT that are delocalized over both L and L'. For molybdenum the T<sub>1</sub> states are <sup>3</sup>MOMo $\delta\delta^*$  whereas for tungsten they are <sup>3</sup>MLCT.



Chart 1 Representative examples of organic and metalloorganic compounds used in solar cell devices.<sup>7-10</sup>

ligand charge transfer (MLCT) transitions as a result of  $M_2\delta$  to ligand  $\pi^*$  interactions. The energy of the MLCT may be tuned by the choice of metal (Mo or W) and by the type of ligand. With an interest in extending these transitions toward the near-infrared and enhancing spectral overlap, we were attracted towards the employment of triphenylamine–cyanoacrylic acid D– $\pi$ –A ligands and report here on the attachment of these ligands LH and L'H shown as I and II respectively below.



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The Ohio State University, 100 West 18th Avenue, Columbus, OH, 43210, USA. E-mail: chisholm@chemistry.ohio-state.edu; Fax: +1 614 292 0368; Tel: +1 614 688 3525 † Electronic supplementary information (ESI) available: Table S1, Fig. S1–S6. CCDC 919555 and 919556. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3sc50322d

LH displays an intense intraligand charge transfer (ILCT) transition from triphenylamine to the cyanoacrylic acid moiety. This transition occurs in the visible region of the spectrum, because the introduction of the cyanoacrylic acid moiety considerably lowers the energy of the  $\pi^*$  molecular orbital (MO). L'H also exhibits an intense ILCT, but it is red shifted relative to that of LH because the thienyl moiety extends the conjugation of the system.<sup>6,12,13</sup> It is anticipated that the incorporation of these ligands into MM quadruply bonded systems will provide two main advantages. First, the relatively low-lying  $\pi^*$  MO will significantly red-shift the energy of the MLCT transition. This may be particularly useful when M = Mo as Mobased MM complexes exhibit higher energy MLCT transitions due to the lower energy of the  $Mo_2\delta$  MO. Second, the MM complexes will exhibit two intense absorption bands in the visible region due to the ILCT and MLCT transitions. This will enhance spectral overlap of these compounds. The synthesis, characterization and photophysical properties of the complexes are reported here.

# **Results and discussion**

#### Syntheses

The reaction between the homoleptic compounds  $M_2(T^iPB)_4$ where M = Mo or W and the respective carboxylic acids ( $\sim 2$ equiv.) 2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid, LH and 5-[4-(diphenylamino)phenyl]thiophene-2-cyanoacrylic acid, L'H in toluene at room temperature lead to the formation of the compounds ML and ML' as microcrystalline precipitates which were collected by centrifugation and washed with toluene and hexanes to remove unreacted  $M_2(T^iPB)_4$ . The molybdenum complexes hereafter abbreviated MoL and MoL' and tungsten complexes, WL and WL', are air-sensitive and highly colored: MoL, red-brown; MoL', brown; WL, green and WL', yellow green. Crystals of MoL suitable for X-ray crystallography were obtained from a concentrated THF solution which was layered with hexanes while crystals of MoL' were obtained by a vapor diffusion of pentane into a THF solution. The compounds were characterized by <sup>1</sup>H NMR spectroscopy and gave molecular ions by MALDI-TOF mass spectrometry. Characterization data are given in the Experimental.

#### Solid-state and molecular structures

The molecular structures of **MoL** and **MoL**' are shown in Fig. 1 and 2, respectively. In both structures we see the *trans*-disposition of the ligands. The aryl groups of the T<sup>i</sup>PB ligands are twisted close to 90° from their attendant carboxylate planes which effectively removes the aromatic ring from conjugation with the M<sub>2</sub> $\delta$  orbital. In contrast the ligands L and L' are arranged in a planar manner so as to maximize L-M<sub>2</sub>-L and L'-M<sub>2</sub>-L' conjugation of the ligand  $\pi$  and M<sub>2</sub> $\delta$  orbitals. Each molecule has a crystallographically imposed center of inversion and in **MoL** the -C<sub>6</sub>H<sub>4</sub>-ligand attached to the cyanoacrylate is seen to extend the conjugation as in the -C<sub>4</sub>H<sub>2</sub>S-group in the **MoL**' complex. In **MoL**' the -C<sub>6</sub>H<sub>4</sub> moiety attached to the diphenylamine group is twisted ~25° from the C<sub>4</sub>S plane. In



**Fig. 1** ORTEP representation of compound **MoL** drawn at 50% probability. Solvent molecules and hydrogens excluded for clarity. Gray = carbon, blue = nitrogen, scarlet = oxygen, green = molybdenum.



Fig. 2 ORTEP representation of compound **MoL**' drawn at 50% probability. Solvent molecules and hydrogens excluded for clarity. Gray = carbon, blue = nitrogen, scarlet = oxygen, yellow = sulfur, turquoise = molybdenum.

both structures the nitrogen atoms of the respective L and L' ligands are planar indicative of the Np $\pi$ -ring conjugation. The central Mo<sub>2</sub>(O<sub>2</sub>C)<sub>4</sub> units are comparable to those seen in numerous carboxylate complexes incorporating the quadruply bonded Mo<sub>2</sub><sup>4+</sup> unit. The structures are also similar to those we have recently proposed for a vinylthienyl carboxylate complex.<sup>14</sup>

#### **Electronic structure calculations**

Electronic structure calculations employing density functional theory and the commercially available Gaussian suite of programs have been performed on the model compounds where formate has been substituted for  $T^{i}PB$ . This saves on computational time and resources and is a reasonable approximation given the lack of aryl group conjugation within the  $T^{i}PB$  ligands as seen from the dihedral angles in the structures of **MoL** and **MoL**'. We refer to the model compounds as *ML* and *ML*'.

The calculated frontier molecular orbitals for the molecules *MoL* and *WL* and their respective energies are shown in Fig. 3. In both molecules the HOMO is an  $M_2\delta$  with extensive mixing with the ligand  $\pi$ -system. This mixing is greater for *MoL* relative to *WL*. This difference arises from the relative energies of the respective  $M_2\delta$  orbitals. The HOMO-1 is an in-phase combination of the ligand-based  $\pi$  orbital that does not have the correct symmetry to interact with the  $M_2\delta$  orbital, while the HOMO-2 is



Fig. 3 Frontier molecular orbitals and calculated energies of MoL and WL.

the out-of-phase ligand  $\pi$  combination which does mix with the  $M_2\delta$  as can be seen in Fig. 3.

Again this mixing is greater for **MoL** than for **WL**. The Mo<sub>2</sub> $\delta$  (HOMO) and the ligand-based filled  $\pi$ -orbitals differ only by ~0.5 eV while the difference in the tungsten complex is ~1.0 eV. Below the HOMO-2 (shown in Fig. 3) come the MM  $\pi$  orbitals (6.7 eV for **MoL** and ~6.0 eV for **WL**) that have minimal interactions with the ligands. The LUMO and LUMO+1 are for both complexes the in-phase and out-of-phase combinations of the

ligand-based  $\pi^*$  orbitals and as can be seen the LUMO+1 mixes with the M<sub>2</sub> $\delta$  orbital. The M<sub>2</sub> $\delta^*$  orbital has minimal mixing with the carboxylate non-bonding  $\pi$  orbitals. The calculated HOMO– LUMO gap is 2.35 eV for *MoL* and 2.08 eV for *WL*.

The calculated frontier orbitals for the complexes MoL' and WL' and their respective energies are given in Fig. 4. The calculations were done in  $C_1$  symmetry and predict for MoL' a near planar geometry involving the thienyl and its neighboring phenyl group. For WL' this extended planarity is not so pronounced and



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it can be seen in the GaussView isosurface contour plots of the respective HOMOs that the Mo<sub>2</sub> $\delta$ -ligand  $\pi$  mixing is greater than its tungsten counterpart. Again this reflects the proximity of the Mo<sub>2</sub> $\delta$  and ligand  $\pi$ -orbital energies. The HOMO-1 and HOMO-2 are the in-phase and out-of-phase ligand  $\pi$ -orbital combinations and again the HOMO-2 has some Mo<sub>2</sub> $\delta$  contribution. Below those orbitals we see that for **MoL**' there are two other ligand  $\pi$  combinations that lie higher than the Mo<sub>2</sub>  $\pi$ -orbitals whereas for **W**L' the W<sub>2</sub>  $\pi$ -orbitals lie directly below the HOMO-2. The LUMO and LUMO+1 are the in-phase and the out-of-phase ligand  $\pi^*$  combinations and the LUMO+2 is the M<sub>2</sub> $\delta^*$  orbital. Clearly the ligands LH and L'H are closely related, as are the electronic

structures of the M<sub>2</sub>-containing complexes. For L', we observe a smaller HOMO–LUMO gap (2.3 eV for *MoL*' and 1.89 eV for *WL*') and a greater mixing with the Mo<sub>2</sub> $\delta$  orbital for L relative to L'.

#### Electronic absorption spectra

The absorption spectra for the free ligand **LH** and the complexes **MoL** and **WL** recorded in THF at room temperature are shown in Fig. 5a. Each compound shows an intense absorption at ~410 nm which we assign to an intraligand  $\pi\pi^*$  charge transfer transition (ILCT). Electronic structure calculations on the free carboxylic acid **LH** indicate that the HOMO is



1.2 а 1.0 Normalized Intensity / a.u. 0.8 0.6 0.4 0.2 0.0 200 1000 1200 1400 Wavelength / nm 1.2 b Normalized Intensity / a.u. 1.0 0.8 0.6 0.4 0.2 0.0 1200 1000 1400 800

Fig. 5 (a) Absorption spectra of LH (purple), MoL, (blue) and WL (red). (b) Absorption spectra of L'H (sky-blue), MoL', (brown-green) and WL' (yellow-green). Taken in THF at room temperature.

principally located on the  $C_6H_4NPh_2$  moiety while the LUMO is polarized toward the cyanoacrylate portion of the molecule. Calculated energies and GaussView isosurface contour plots of the frontier orbitals of **LH** and **L'H** are given in the ESI (Fig. S1†). Occurring to lower energy in the metal containing complexes are broad and intense absorptions associated with the  $M_2\delta$  to ligand  $\pi^*$  MLCT. The absorption spectrum of **WL** has a  $\lambda_{max} \sim$ 900 nm which shows evidence of a vibronic feature with an energy separation of ~1500 cm<sup>-1</sup> and a long tail toward higher energy. Similar spectral features were seen for the complex *trans*-W<sub>2</sub>(T<sup>i</sup>PB)<sub>2</sub>(O<sub>2</sub>CCH=CHC<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>.<sup>14</sup>

The absorption spectra for L'H, MoL' and WL' recorded in THF at room temperature are shown in Fig. 5b and show parallel features to those described above. There is an ILCT transition at ~450 nm which is relatively unchanged in energy in the metal containing complexes (a slight bathochromic shift is seen for WL'). To lower energy we see the <sup>1</sup>MLCT transitions at 600 nm for MoL' and ~1000 nm ( $\lambda_{max}$ ) for WL'. Again for WL' we see evidence of vibronic features and an extensive tailing of the <sup>1</sup>MLCT into the visible region of the spectrum.

#### Steady state emission

The steady state emission spectra for all four compounds were recorded at room temperature in THF. (Fig. 6) The emission spectra of **MoL**' and **WL** were also measured at 77 K in 2-methyltetrahydrofuran. Compound **MoL** shows dual emission with peaks at  $\sim$ 720 and 1100 nm upon excitation at 600 and 658 nm respectively. Based on its small Stokes shift the peak at 720 nm is assigned to fluorescence from the <sup>1</sup>MLCT. Previous

**Fig. 6** (a) Fluorescence (solid blue,  $\lambda_{exc} = 600$  nm) and phosphorescence (dashed blue,  $\lambda_{exc} = 658$  nm) spectra of **MoL** and emission spectra of **MoL**' at room temperature (solid brown-green,  $\lambda_{exc} = 658$  nm) and 77 K (dashed brown-green,  $\lambda_{exc} = 658$  nm). (b) Emission spectra of **WL** at room temperature (red,  $\lambda_{exc} = 658$  nm,) and 77 K (dashed red,  $\lambda_{exc} = 658$  nm) and **WL**' at room temperature (yellow-green,  $\lambda_{exc} = 785$  nm).

Wavelength / nm

studies on molybdenum complexes and the large Stokes shift allow the band at 1100 nm to be assigned to phosphorescence from the <sup>3</sup>MoMo $\delta\delta^*$ . (Fig. 6a) **MoL**' shows a broad emission band that extends from the visible into the infrared. This band starts at ~650 and shows peaks at ~940, 1080 and 1270 nm. Upon cooling to 77 K the relative intensity of the band at 1080 increases and vibronic features are observed. The vibronic spacing was determined to be ~330 cm<sup>-1</sup>. This result indicates that the broad band extending from ~650 to 1400 nm consists of two bands. The band with a peak at ~940 is assigned to fluorescence from the <sup>1</sup>MLCT and the band that is centered at 1080 nm is due to phosphorescence from the <sup>3</sup>MoMo $\delta\delta^*$ .

WL shows a broad emission extending from ~850 to above 1400 nm with a peak at ~960 nm and evidence of vibronic features. When cooled to 77 K the vibronic features are better resolved and the vibronic spacing is determined to be ~1200 cm<sup>-1</sup>. WL' also shows a broad emission extending from ~920 to above 1500 nm with a peak at ~1100 nm and vibronic features with a spacing of ~1200 cm<sup>-1</sup>. Based on the small Stokes shift and vibronic spacing the emission from WL and WL' are assigned as fluorescence from the <sup>1</sup>MLCT state. No phosphorescence was observed from WL and WL' within the detection window. This is likely due to non-radiative decay. The triplet states were however detected with time-resolved spectroscopy, *vide infra*.

#### Electrochemistry

In THF solutions, the four compounds under consideration all show reversible one electron oxidation waves by cyclic

Table 1 Electrochemical data for compounds MoL, MoL', WL and WL'<sup>a</sup>

 $^a$  The redox potentials are referenced to the  $\rm Cp_2Fe^{+/0}$  couple.

voltammetry. This corresponds to removal of an electron from the  $M_2\delta$  orbital. The molybdenum complexes have oxidation potentials close to the  $Cp_2Fe^{0/+}$  couple while those of the tungsten complexes fall close to -0.5 V vs.  $Cp_2Fe^{0/+}$ . Upon reduction all complexes show evidence of a ligand-based one electron reduction wave which is quasi-reversible and the tungsten complexes show evidence of a second reduction wave which is irreversible. The electrochemical data are summarized in Table 1 and the cyclic voltammograms are shown in the ESI (Fig. S2<sup>†</sup>). Of note is the fact that the first reduction wave occurs at lower negative potentials for **WL** and **WL**' than their respective molybdenum complexes.

#### Time-resolved spectroscopic studies

Femtosecond transient absorption spectra. For all four compounds, the properties of both  $S_1$  and  $T_1$  excited states have been examined by ultrafast spectroscopic techniques in order to

obtain information pertaining to their lifetimes and where electron density resides in these states. Results from the TA data detailed below are well complemented by fs-TRIR studies presented in the following section. All compounds were excited into the <sup>1</sup>MLCT band in THF solutions, and kinetic traces are shown in ESI Fig. S3.<sup>†</sup>

In the fs-TA spectra of **MoL** (Fig. 7a), a prominent  $S_1 \rightarrow S_n$ absorption is observed at 470 nm; however, it is likely that this band extends out to lower energies where it is obscured by the MLCT ground state (GS) bleach (500-600 nm). Also present is a bleach at 410 nm from the <sup>1</sup>ILCT transition associated with the acrylate ligand. In the S1 state, electron density is largely located on the cyanoacrylate portion of the ligand, preventing charge transfer from the triphenylamine unit and leading to depletion of the ILCT. The recovery of the bleach coincides with the decay of the singlet absorption, giving a singlet lifetime of 7.1 ps. As noted above, the triplet state is MoModo\* in nature, which should not greatly affect the ILCT transition. The 410 nm band is no longer depleted in the T<sub>1</sub> state, however the <sup>1</sup>MLCT GS bleach is apparent at  $\sim$ 550 nm along with a T<sub>1</sub>  $\rightarrow$  T<sub>n</sub> absorption at 465 nm. The triplet state does not decay on the timescale of this experiment and it has been further characterized by ns-TA along with MoL'.

The features of the spectra for **MoL**' (Fig. 7b) are similar to those described above though the bands are shifted to lower energy in accordance with the stabilization of L'  $\pi^* \nu s$ . L  $\pi^*$ . In the <sup>1</sup>MLCT state, a bleach of the intraligand CT state occurs at 460 nm while  $S_1 \rightarrow S_n$  absorptions are observed at 565 and



Fig. 7 fs-TA spectra of (a) MoL,  $\lambda_{ex} = 675$  nm; (b) MoL',  $\lambda_{ex} = 675$  nm; (c) WL,  $\lambda_{ex} = 800$  nm and (d) WL',  $\lambda_{ex} = 800$  nm; recorded in THF at RT.

510 nm. An isosbestic point (485 nm) is also observed during decay of the singlet state ( $\tau = 9.0 \pm 0.2$  ps), indicating direct conversion to the <sup>3</sup>MoMoδδ\* state. Following this process, a  $T_1 \rightarrow T_n$  absorption at 490 nm and GS bleach to lower energy persist throughout the duration of the experiment.

For WL, the initial spectra are dominated by broad singlet state absorption from 450-650 nm with peaks at 470 and 555 nm. As for MoL, the ILCT bleach is present at 410 nm. The  $S_1 \rightarrow S_n$  absorption also occurs at similar energies for the two compounds since this should largely be a L  $\pi \rightarrow$  L  $\pi^*$  transition. The lowest readily accessible pump wavelength for the tungsten compounds was 800 nm which injects excess energy into the complex. Consequently, a noticeable cooling of the 555 nm peak at early times ( $\tau \sim 0.5 \text{ ps}$ ) is observed. The lifetime of the <sup>1</sup>MLCT state of WL is 16.3 ps, much longer than any of the other compounds investigated even though the heavier element tungsten is present. We have been interested in determining the factors that contribute to excited state lifetimes with one possible component being the separation of the electron and hole. Supported by the fs-TRIR data, vide infra, the electron may be separated further from the metal center in WL thereby slowing its recombination. After decay to the <sup>3</sup>MLCT state, a lower intensity, broad absorption remains with  $\lambda_{max} = 545$  nm. Though the GS MLCT bleach is not visible in this region, the ILCT bleach remains as this transition is still affected in the <sup>3</sup>MLCT state. A longer decay component ( $\tau < 3$  ns) is observable in the data which can be attributed to decay of the triplet state. Ditungsten tetracarboxylate <sup>3</sup>MLCT lifetimes are typically short (3-10 ns) in quadruply bonded metal carboxylates,<sup>15</sup> and the low energy of this state in WL enhances the rate of GS repopulation.

Finally, WL' (Fig. 7d) displays many of the same excited state properties as those previously detailed. Following 800 nm excitation, a broad  $S_1 \rightarrow S_n$  absorption peaks at 540 nm and tails into the near IR. The position of this band is similar to that of MoL', again indicating the transient absorption is mainly ligand localized. The decay of this band coincides with recovery of the ILCT state bleach (470 nm), giving rise to an isosbestic point at 490 nm and a <sup>1</sup>MLCT lifetime of 8.8 ps. The <sup>3</sup>MLCT T<sub>1</sub> absorption appears broad and shifted to lower energy ( $\lambda_{max} \sim$ 600 nm), however it decays almost completely during the timeframe of the experiment leading to an estimation of the triplet lifetime as 1 ns. The rapid decay is again due to the small energy gap between T<sub>1</sub> and the ground state which enhances the rate of radiationless decay. The ILCT bleach is also present in the <sup>3</sup>MLCT state and decays on the same timescale, producing a second isosbestic point at 465 nm.

Nanosecond transient absorption spectra. Though the triplet states of the tungsten compounds are not long-lived enough to be studied by ns-TA, the technique can be used for **MoL** and **MoL'**. The spectra of **MoL** (Fig. 8a) show bleaches at 380 and 560 nm and a transient absorption at ~440 nm. The T<sub>1</sub> lifetime obtained from decay of this band (average of 54 µs) is in agreement with the lifetime of T<sub>1</sub> states in previously studied molybdenum complexes<sup>15</sup> and is assigned to the <sup>3</sup>MoMoδô\* state. The kinetic trace is shown in Fig. S4.† Presently, it is unclear why the ILCT state remains bleached in this triplet state where the excited electron now resides in a  $\delta$ -antibonding



Fig. 8 (a) ns-TA spectra of MoL recorded at 1  $\mu$ s (closed) and 50.5  $\mu$ s (open) (b) ns-TA spectra of MoL' recorded at 0.04  $\mu$ s (closed) and 1.4  $\mu$ s (open).

orbital. This observation may be related to the continued growth of the MLCT GS bleach at long times during the fs experiment.

The **MoL**' spectra are qualitatively similar to those at long times in the fs experiment and show an absorption at ~510 nm and a bleach at 620 nm. Kinetics obtained from these bands give an average T<sub>1</sub> lifetime of 2.5  $\mu$ s which is roughly an order of magnitude shorter than lifetimes commonly seen for <sup>3</sup>MoMoδδ\* states.<sup>15</sup> The low energy of the <sup>1</sup>MLCT state (S<sub>0-0</sub> ~ 12 500 cm<sup>-1</sup>) means it is possible for the <sup>3</sup>MLCT state to be very near in energy to <sup>3</sup>MoMoδδ\* (~9100 cm<sup>-1</sup>). <sup>3</sup>MLCT states are known to be shorter-lived and the proximity may enable more efficient decay back to the ground state.

**Time-resolved infrared spectra.** Each of the compounds has been examined by fs-TRIR spectroscopy in THF solution with excitation into the <sup>1</sup>MLCT absorptions. Spectra were collected in the region of the C $\equiv$ N vibration (2280–2080 cm<sup>-1</sup>) as well as in lower energy regions (1650–1350 cm<sup>-1</sup>) where organic ligand vibrations occur. Kinetic traces are given in ESI Fig. S5.† First, the **MoL** and **WL** compounds will be compared (Fig. 9). In **MoL**, a weak transient signal is observed at 2168 cm<sup>-1</sup> which we assign to  $\nu$ (CN) of the acrylate ligand L. This is shifted 52 cm<sup>-1</sup> to lower energy relative to the ground state. The absorption disappears on conversion to the triplet state, consistent with the



Fig. 9 fs-TRIR spectra of (a) MoL,  $\lambda_{ex}=675$  nm; and (b) WL,  $\lambda_{ex}=800$  nm; recorded in THF at RT.

assignment of  $T_1$  as <sup>3</sup>MoMo\delta\delta\* which should not greatly affect the cyano stretch. In the lower energy region, we observe several new IR bands associated with both the S<sub>1</sub> and T<sub>1</sub> states. Bleaches at 1510 and 1585 cm<sup>-1</sup> can be assigned to the ground state  $v_{as}(CO_2)$  and v(C=C) of L, respectively, as supported by DFT calculations. We propose that the intense absorption in the  $S_1$  state at 1480 cm<sup>-1</sup> is predominantly the  $v_{as}(CO_2)$  mode while the S<sub>1</sub> band at 1530 cm<sup>-1</sup> arises from  $\nu$ (C=C). Upon photoexcitation the L  $\pi^*$  orbital is populated leading to a reduction in bond strength and a weaker stretching frequency for these vibrations. It is not presently clear how to assign the absorptions at 1590 in the S<sub>1</sub> state, but it is likely associated with ring vibrations of the TPA moiety. In the long lived spectra assigned to the T<sub>1</sub> state, the absorption at 1540 cm<sup>-1</sup> is due to  $v_{as}(CO_2)$  of the <sup>3</sup>MoMoδδ\* state for the reasons outlined in previous TRIR studies of related carboxylates.15 Based on DFT calculations, the bands ~1400 cm<sup>-1</sup> may be attributed to  $\nu_s(CO_2)$  of L.

In contrast to its molybdenum counterpart, **WL** exhibits an intense IR absorption at 2184 cm<sup>-1</sup> assignable to  $\nu$ (CN) in the <sup>1</sup>MLCT state. The 41 cm<sup>-1</sup> shift to lower energy from the ground state is smaller than the shift observed with **MoL**, suggesting this singlet state is spread over more of the ligand and is less concentrated on the cyano portion. As noted in the fs-TA, this increased delocalization may also contribute to the longer S<sub>1</sub> lifetime of **WL**. The band decays with the singlet state but leaves a weaker C=N vibration at 2190 cm<sup>-1</sup> which we can readily assign to  $\nu$ (CN) in the <sup>3</sup>MLCT state. This is notably weaker than the  $\nu$ (CN) of the S<sub>1</sub> state, in part due to the lower population of the T<sub>1</sub> state following singlet decay. However, it is not entirely

clear what determines the relative intensities of the excited state vibrations such as why  $\nu$ (CN) is so much more prominent for **WL** relative to **MoL**. What can be seen is that  $\nu$ (CN) shifts to higher energy in the T<sub>1</sub> state relative to the S<sub>1</sub> state, which we propose is associated with the charge on the ligand being further removed from the CN group, namely toward the aromatic centers. We note, for example, that the S<sub>1</sub> lifetime for the compound *trans*-W<sub>2</sub>(T<sup>i</sup>PB)<sub>2</sub>(O<sub>2</sub>CC=C-9-anthracene)<sub>2</sub> is also longer that its dimolybdenum counterpart.<sup>14</sup> Evidence has been given that the ligand centered electron is more spatially removed from the hole on the W<sub>2</sub> center and in the triplet state lies predominantly on the anthracene moiety.<sup>16</sup>

The lower energy portion of the spectrum is much less intense in Fig. 9b and an expanded section of this spectrum is shown in the ESI Fig. S6.<sup>†</sup> Again we see bleaches assignable to C=C and  $-CO_2$  vibrations at 1570 and 1505 cm<sup>-1</sup>, as well as a shift of these modes to lower energy (1550 cm<sup>-1</sup>, 1480 cm<sup>-1</sup>) in the <sup>1</sup>MLCT state. We also note that the long-lived state does not show  $\nu_{as}(CO_2) \sim 1540$  cm<sup>-1</sup> that is more characteristic of a <sup>3</sup> $\delta\delta^*$  state.<sup>17</sup>

The TRIR spectra of the compounds containing ligand L' (Fig. 10) present many features similar to those described above. For **MoL**', we again observe a weak C=N stretch in the <sup>1</sup>MLCT state at 2170 cm<sup>-1</sup> ( $\Delta\nu$ (CN) = -49 cm<sup>-1</sup>). The lower energy region displays ground state bleaches associated with L' C=C and asymmetric -CO<sub>2</sub> vibrations at 1585 and 1505 cm<sup>-1</sup>, along with prominent <sup>1</sup>MLCT absorptions shifted ~30 cm<sup>-1</sup> to lower energy from the GS frequencies. With a lifetime of 7 ps, the C=N band and intense ligand vibrations at 1550 and 1480



Fig. 10 fs-TRIR spectra of (a) MoL',  $\lambda_{ex} = 675$  nm; and (b) WL',  $\lambda_{ex} = 800$  nm; recorded in THF at RT.

cm<sup>-1</sup> disappear, causing L'  $\nu_{as}(CO_2)$  of the <sup>3</sup>MoMo $\delta\delta^*$  state to become visible at 1540 cm<sup>-1</sup>.

In the spectra of the related compound **WL**', the intense  $\nu$ (CN) absorption of the <sup>1</sup>MLCT state is observed at 2177 cm<sup>-1</sup>, a shift of 48 cm<sup>-1</sup> from the ground state at 2225 cm<sup>-1</sup>. As was seen in the TRIR of **WL**, this band moves slightly to higher energy (2182 cm<sup>-1</sup>) in the longer-lived T<sub>1</sub> state. Ligand vibrations in the S<sub>1</sub> state initially appear similar to those observed for **MoL**', but with time these decay and the region is relatively silent in the <sup>3</sup>MLCT state. This observation, along with the weakness of the C≡N stretch in the triplet state, can be attributed to rapid decay of the T<sub>1</sub> state in accordance with the energy gap law, as supported by the TA data.

One question frequently raised in studying MLCT states of molecules of this type is whether the excited state electron density is located on one of the ligands or delocalized over both. In the case of heavily studied  $[Ru(bpy)_3]^{2+}$ -type complexes the charge is localized on a single ligand,18,19 while we have found examples of both limiting cases in previous investigations of excited state mixed valence.<sup>20</sup> In the present study we note that only one  $\nu(CN)$  is observed in the excited MLCT states for all four compounds, while we might expect to see two IR active CN stretches if the environment of each ligand was notably different. In addition, calculations on the anions of the model complexes  $[ML]^-$  and  $[ML']^-$  predict  $\nu(CN)$  to shift to lower energy by  $\sim 50 \text{ cm}^{-1}$  for L and 25 cm<sup>-1</sup> for L'. In these calculations the charge is delocalized over both ligands and the electron formally occupies the LUMO of the MO configuration of the neutral molecules. The observed values of  $\nu(CN)$  in the excited state fall close to the calculations and are not vastly larger, as was seen for the compounds  $trans-M_2(O_2CMe_2)_2$ -[(N<sup>i</sup>Pr)<sub>2</sub>CC=C-Ph]<sub>2</sub> which have localized MLCT states.<sup>20</sup> Thus we propose that the MLCT states of the four compounds reported here have the photo-excited electron delocalized over both L and L'.

## Conclusion

The attachment of the push-pull aminocyanoacrylate ligands to the MM quadruply bonded centers allows the MLCT absorption spectra to be extended well into the near IR with intense ILCT bands in the visible. These absorptions are intense and the MLCT bands have strong tails to higher energy. The S<sub>1</sub> states have relatively long lifetimes, ~10 ps, when compared with most transition metal <sup>1</sup>MLCT states that undergo inter-system crossing within 100 fs to triplet states. These two features suggest that these compounds should find applications as photon harvesters and this is the topic of on-going research.

# **Experimental**

#### **General procedures**

The reactions (with the exception of ligand syntheses) were conducted under inert atmosphere (argon or nitrogen) using standard glovebox and Schlenk techniques and solvents used in these reactions were dried and distilled by standard methods and degassed before use.  $Mo_2(T^iPB)_4$  (ref. 21) and  $W_2(T^iPB)_4$  (ref. 22) were prepared by reported procedures. NMR spectra were recorded on a 400 MHz Bruker DPX Advance 400 spectrometer. All <sup>1</sup>H NMR chemical shifts are in ppm relative to the protio impurity in tetrahydrofuran (THF)- $d_8$  at 3.58 ppm.

#### Electronic absorption spectra

UV-Vis-NIR electronic spectra in THF solutions were measured at room temperature using a Perkin-Elmer Lambda 900 spectrometer using a 1 cm  $\times$  1 cm quartz cuvette sealed with a Kontes top.

#### **Electrochemical studies**

Cyclic voltammograms were collected at a scan rate of 50 mV s<sup>-1</sup> using a Princeton Applied Research (PAR) 173A potentiostatgalvanostat equipped with a PAR 176 current-to-voltage converter. The measurements were performed under an argon atmosphere in a 0.1 M solution of  ${}^{n}Bu_{4}NPF_{6}$  in THF inside a single-compartment voltammetry cell that was equipped with a platinum wire auxiliary electrode, a platinum working electrode and a pseudoreference electrode consisting of a silver wire in 0.1 M  ${}^{n}Bu_{4}NPF_{6}$ -THF separated from the bulk solution by a Vycor tip. The potentials are referenced to the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> couple.

#### Mass spectrometry

Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Microflex mass spectrometer. Dithranol was used as the matrix.

#### **Electronic structure calculations**

The model complexes were optimized in the gas-phase using density functional theory (DFT) utilizing the Gaussian09 suite of programs.<sup>23,24</sup> The B3LYP functional<sup>25,26</sup> was used in conjunction with the SDD energy consistent pseudopotentials and the SDD energy consistent basis set for molybdenum and tungsten<sup>27</sup> and the 6-31G\* basis set for H, C, N, O and S atoms. Vibrational frequency analysis was used to confirm that the optimized structures were minima on the potential energy surface. GaussView isosurface contour plots are shown with an isovalue of 0.02.<sup>26</sup> Electronic absorption spectra were calculated using the time dependent DFT (TDDFT) method.

#### Crystallographic information

Single crystals of **MoL** and **MoL**' were isolated as red-brown and brown crystals respectively and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo K $\alpha$  radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack.<sup>28</sup> The structures were solved by the direct methods program in SHELXS-97. Full-matrix least-squares refinements based on  $F^2$ were performed in SHELXL-97,<sup>29</sup> as incorporated in the WinGX package.<sup>30</sup> For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with  $U({\rm H}) = 1.5 U_{\rm eq}$  (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with  $U({\rm H}) = 1.2 U_{\rm eq}$  (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.<sup>31</sup>

One of the isopropyl moieties on the T<sup>i</sup>PB moiety of **MoL**' was disordered over two positions and modeled accordingly. In both **MoL** and **MoL**' there was evidence of severely disordered solvent in the lattice that was difficult to model sufficiently. In the case of **MoL**' this electron density was quite diffuse and removed using the SQUEEZE<sup>32</sup> command in PLATON<sup>33</sup> which excluded 33 e<sup>-</sup> from a void of 162 Å<sup>3</sup> which roughly corresponds to one THF molecule. In the case of **MoL** the disordered THF molecule was able to be found in the difference map, but had notably high *U* values and required numerous restraints and constraints. Modeling of this THF molecule in multiple locations was unsuccessful and after several attempts refinement remained unstable. Ultimately the SQUEEZE command was employed and excluded 43 e<sup>-</sup> (THF) from a void of 290 Å<sup>3</sup>.<sup>†</sup>

#### Femtosecond transient absorption measurements

Femtosecond transient absorption (fsTA) experiments were carried out using laser and detection systems that have been previously described.34 The molybdenum samples were excited at 675 nm and the tungsten samples at 800 nm (with excitation power of 1–2  $\mu$ J at the sample) by the output of an optical parametric amplifier (OPA) equipped with a harmonics attachment (UV/Vis). During the measurements the samples were kept in constant motion by manual movement of an XYZ stage in the vertical and horizontal directions. To ensure that no photodecomposition occurred during data collection, absorption spectra were recorded before and after the TA measurements. The measurements were repeated several times at each of the pump-probe delay positions to confirm data reproducibility throughout the experiment, and the resulting spectra were corrected for the chirp in the white-light continuum.35 Kinetics were fit in general to a sum of exponential decay components of the form  $S(t) = \Sigma_i A_i \exp(-t/\tau_i) + C$ , with amplitudes  $A_i$ , lifetime,  $\tau_i$ , and offset, *C*, using Microcal Origin 6.0. Error bars for the lifetime are reported as the standard error of the fit.

#### Nanosecond transient absorption measurements

Nanosecond transient absorption (nsTA) experiments were carried out systems that have been previously described.<sup>36</sup> Measurements were carried out in  $1 \times 1$  cm<sup>2</sup> quartz cuvettes equipped with Kontes stopcocks. Nanosecond transient absorption spectra were measured on a home-built instrument pumped by a frequency-tripled (355 nm) Spectra-Physics GCR-150 Nd:YAG laser (fwhm 8 ns, 5 mJ per pulse). The signal from the photomultiplier tube (Hamamatsu R928) was processed by a Tektronics 400 MHz oscilloscope (TDS 380).

#### Time-resolved infrared measurements

The time-resolved infrared (TRIR) experiment utilizes a Ti:Sapphire oscillator and regenerative amplifier combination operating at 1 kHz that has been previously described.<sup>37</sup> The

fundamental laser beam is split to pump an OPA equipped with either an SFG or SHG attachment to produce pump pulses tunable throughout the visible spectrum and an OPA with a difference frequency attachment to produce mid-IR pulses (2– 10  $\mu$ m). The IR beam is split into a probe and a reference beam by a Ge beamsplitter. These beams then pass through the sample, where the pump beam is overlapped with the probe, and are directed into a Triax 320 spectrometer. The probe and reference are spectrally dispersed onto separate HgCdTe array (32 element) detectors cooled by liquid nitrogen. The pump and probe pulses are synchronized by passing the pump through a chopper operating at 500 Hz, allowing for measurement of the probe signal under pump on/off conditions. Signal from the reference beam is subtracted to obtain the overall signal.

Samples were sealed in a Perkin-Elmer rectangular semidemountable cell with a 1.0 mm Teflon spacer between a 4 mm and a 2 mm CaF<sub>2</sub> window. Solutions were prepared in a glove box with THF as the solvent such that the absorbance at the MLCT  $\lambda_{max}$  was 1.0–2.0. The molybdenum samples were excited at 680 nm and the tungsten samples at 800 nm. The excitation power at the sample was kept at ~1  $\mu$ J. The static sample cell was manually translated with an XYZ stage between scans to ensure photo-decomposition was not an issue. The spectra shown consist of multiple experiments covering a wide range of IR probe energies. Gaps present in the spectra are due to the probe wavelengths not overlapping between experiments.

#### Steady state emission spectra

The steady-state visible luminescence spectra between 290 and 840 nm were acquired on a SPEX Fluoromax-2 spectrofluorometer. The room temperature data were taken using THF as the solvent while 2-methyltetrahydrofuran was used as the solvent for measurements done at 77 K. The steady-state near-IR luminescence spectra were measured on a home-built instrument utilizing a germanium detector. Compounds **MoL**, **WL** and **MoL**' were excited at 658 nm and compound **WL**' was excited at 785 nm (laser diode max power: 65 mW).

#### Syntheses

2-Cyano-3-(4-(diphenylamino)phenyl)acrylic acid (LH). 4-Diphenylaminobenzaldehyde was prepared by a Vilsmeier formylation reaction between triphenylamine, dimethylformamide (DMF) and POCl<sub>3</sub>. This was followed by the Knoevenagel condensation of the monoaldehyde with cyanoacetic acid in the presence of piperidine to yield LH.<sup>12</sup>

5-[4-(Diphenylamino)phenyl]thiophene-2-cyanoacrylic acid (L'H). Triphenylamine was brominated with *N*-bromosuccinimide to yield 4-(diphenylamino)bromobenzene.<sup>38</sup> A Stille coupling between 2-(tributylstannyl)thiophene and 4-(diphenylamino)bromobenzene yielded 2-[4-diphenylamino)phenyl] thiophene.<sup>39</sup> This compound was formylated by means of the Vilsmeier formylation reaction using an adapted procedure. Briefly, DMF (0.47 mL, 6.11 mmol) was cooled to 0 °C in an ice bath and then POCl<sub>3</sub> (0.30 mL, 3.05 mmol) was added dropwise. The reaction temperature was increased to 30 °C and 2-[4-(diphenylamino)phenyl]thiophene (0.500 g, 1.53 mmol) was added in one portion. The reaction mixture was then heated to 45–50 °C and stirred for 3 hours. The mixture was poured onto ice and sodium hydroxide was added until a pH of 10–11 was reached. It was then extracted with dichloromethane, dried over magnesium sulfate and concentrated under vacuum to yield a dark yellow residue. The residue was purified *via* column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>–hexanes, 4 : 1 v/v) to yield 5-[4-(diphenylamino)phenyl]formyl-thiophene-2-yl as a dark yellow oil<sup>12</sup> (yield: 40%). This was followed by a Knoevenagel condensation of the monoaldehyde with cyanoacetic acid to yield  $L'H^{13}$  (yield: 74%).

 $Mo_2(T^iPB)_2[O_2CC(CN) = CH-C_6H_4-NPh_2]_2$  (MoL). A solution of  $Mo_2(T^iPB)_4$  (0.185 g, 0.156 mmol) in toluene (*ca*. 5 mL) was added to a suspension of LH (0.098 g, 0.288 mmol) in toluene (*ca*. 5 mL). A brown reaction mixture was formed. The reaction was stirred for 3 days. The solid was collected by centrifugation and washed twice with toluene (*ca*. 5 mL) and once with hexanes (*ca*. 10 mL) to yield a red-brown powder. Crystals were grown by layering a saturated THF solution with hexanes. (Yield: 60%) NMR (THF-d<sub>8</sub> 400 MHz): 8.36 (s, 2H), 8.07 (d, 4H) 7.43 (m, 8H), 7.29 (m, 8H), 7.27 (m, 4H), 7.14 (s, 4H), 7.10 (d, 4H), 3.24 (septet, 4H), 2.97 (septet, 2H), 1.32 (d, 36H). UV-Vis (THF, 298 K) 569, 412, 291, 262 nm. MALDI-TOF: found: 1365, M<sup>+</sup>. Calculated: 1371.

 $W_2(T^iPB)_2[O_2CC(CN)=CH-C_6H_4-NPh_2]_2$  (WL). A solution of  $W_2(T^iPB)_4$  (0.220 g, 0.162 mmol) in toluene (*ca.* 5 mL) was added to a suspension of LH (0.098 g, 0.289 mmol) in toluene (*ca.* 5 mL). A green suspension was formed. The reaction was stirred for 3 days. The solid was collected by centrifugation and washed twice with toluene (*ca.* 5 mL) and once with hexanes (*ca.* 10 mL) to yield a green powder. (Yield: 54%) NMR (THF-d<sub>8</sub> 400 MHz): 7.90 (d, 4H), 7.62 (s, 2H), 7.41 (m, 8H), 7.27 (m, 8H), 7.21 (m, 4H), 7.13 (m, 8H), 2.99 (m, 6H), 1.31 (d, 12H), 1.27 (d, 24H). UV-Vis (THF, 298 K) 900, 422, 289, 262 nm. MALDI-TOF: found: 1544, M<sup>+</sup>. Calculated: 1540.

 $Mo_2(T^iPB)_2[O_2CC(CN) = CH-C_4H_2S-C_6H_4-NPh_2]_2$  (MoL'). A solution of  $Mo_2(T^iPB)_4$  (0.135 g, 0.114 mmol) in toluene (*ca.* 5 mL) was added to a suspension of L'H (0.090 g, 0.213 mmol) in toluene (*ca.* 5 mL). A dark green suspension was formed. The reaction was stirred for 3 days. The solid was collected by centrifugation and washed twice with toluene (*ca.* 5 mL) and once with hexanes (*ca.* 10 mL) to yield a brown powder. Crystals were grown through vapor diffusion of pentane into a THF solution. (Yield: 45%) NMR (THF-d<sub>8</sub> 400 MHz): 8.57 (s, 2H), 8.11 (d, 2H), 7.74 (d, 4H), 7.71 (d, 2H), 7.38 (m, 8H), 7.14 (m, 16H), 7.02 (m, 4H) 3.02 (m, 6H), 1.29 (d, 12H), 1.09 (d, 24H). UV-Vis (THF, 298 K) 609, 457, 303 nm. MALDI-TOF: found: 1530, M<sup>+</sup>. Calculated: 1533.3.

**W**<sub>2</sub>(**T**<sup>i</sup>**PB**)<sub>2</sub>[**O**<sub>2</sub>**CC**(**CN**)=**CH-C**<sub>4</sub>**H**<sub>2</sub>**S-C**<sub>6</sub>**H**<sub>4</sub>-**NPh**<sub>2</sub>]<sub>2</sub> (**WL**'). A solution of W<sub>2</sub>(**T**<sup>i</sup>**PB**)<sub>4</sub> (0.184 g, 0.136 mmol) in toluene (*ca.* 5 mL) was added to a suspension of **L**'**H** (0.074 g, 0.174 mmol) in toluene (*ca.* 5 mL). A yellow green suspension was formed. The reaction was stirred for 3 days. The solid was collected by centrifugation and washed twice with toluene (*ca.* 5 mL) and once with hexanes (*ca.* 10 mL) to yield a yellow green powder. (Yield: 34%) NMR (THF-d<sub>8</sub> 400 MHz): 7.72 (s, 2H) 7.66 (s, 2H), 7.64 (s, 2H), 7.60 (d, 4H), 7.34 (m, 8H), 7.17 (m, 12H), 7.13 (m, 8H) 3.0 (m, 6H), 1.30 (d, 12H), 1.27 (d, 24H). UV-Vis (THF, 298 K) 1004, 465, 301 nm. MALDI-TOF: found: 1704.6, M<sup>+</sup>. Calculated: 1705.

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