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Introduction

Arylboron compounds have attracted considerable attention for their photophysical properties.¹ Notably, the strong emission spectra associated with arylboranes can be quenched upon addition of ions such as F^- or CN^- which can bind to the Lewis acidic center.^{2,3} Their spectral features can thus be employed in sensors and various other applications where fluorescence is sensitive. The molecule referred to as BODIPY, shown below, is a prime example of an arylboron compound showing such spectral features.

F F BODIPY

cyanoacrylate,⁵ α, α' -thienylcarboxylates⁶ or a 2,6-azulenecarboxylate ester.⁷ In these compounds the *trans*-L-M₂-L geometry as seen in Fig. 1 allows for extensive L π -M₂ δ -L π conjugation which results in the extended planar structure being thermodynamically favored.

Modulating the $M_2\delta$ -to-ligand charge transfer

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shifted to much higher energy in a reversible manner for M = Mo.

transition by the use of diarylboron substituents†

From the reactions between the quadruply bonded complexes $M_2(T^{i}PB)_{4}$, where M = Mo or W and $T^{i}PB$ =

2,4,6-triisopropylbenzoate, and the carboxylic acids $HOOC-C_6H_4-4-B(mesityl)_2$, LH (2 equivalents) the complexes *trans*- $M_2(T^iPB)_2L_2$ have been prepared. The new compounds have been characterized by ¹H NMR, MALDI-TOF MS, UV-Vis-NIR and steady-state emission spectroscopy, time-resolved transient absorption spectroscopy and cyclic voltammetry. These results are compared with the related properties of the benzoates, $M_2(T^iPB)_2(O_2CPh)_2$ (prepared similarly) and with DFT calculations on model compounds where formate substitutes for TⁱPB. The new compounds $M_2(T^iPB)_2L_2$ are intensely colored in toluene or

THF solutions: red (M = Mo) and green (M = W) and the introduction of the p-B(mesityl)₂ group notably

shifts these metal to ligand charge transfer transitions to lower energy in comparison to the benzoate

complexes $M_2(T^iPB)_2(O_2C-C_6H_5)_2$. Upon the addition of fluoride ions these intense absorptions are

A simple frontier orbital energy diagram is shown in Fig. 2, which shows how the $M_2\delta$ orbital interacts with only the outof-phase π^* combination of the ligand π^* systems causing a splitting of the in- and out-of-phase combinations of the $L\pi^*$. In D_{2h} symmetry the $M_2\delta$ to in-phase $L\pi^*$ combination, which is typically the HOMO \rightarrow LUMO transition, is a fully allowed MLCT transition and this occurs in the visible or NIR region of

Work in this lab has recently focused on the photophysical properties of carboxylate ligands attached to MM quadruply bonded centers and in particular to the metal-to-ligand charge transfer states of compounds of the form $trans-M_2(T^iPB)_2L_2$ where $L = a \pi$ -acceptor ligand such as cyanobenzoate,⁴

 $[\]dagger$ Electronic supplementary information (ESI) available. CCDC 943288. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3dt51684a



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Fig. 2 $M_2\delta$ orbital interaction with the in-phase and out-of-phase combinations of the ligand π^\star orbitals.

the spectrum. We are interested in investigating the influence of introducing a BAr₂ group to a simple π -acceptor ligand such as benzoate and we report here results that were prompted by this line of inquiry.

Results and discussion

Syntheses

The synthesis of the boron containing carboxylic acid and its reaction to form the new compounds $trans-M_2(T^iPB)_2L_2$, where M = Mo, compound I and M = W, compound II, are shown in Scheme 1.

The benzoate complexes *trans*- $M_2(T^iPB)_2(Bz)_2$, where $Bz = O_2CPh$, were similarly prepared from the reactions between $M_2(T^iPB)_4$ and benzoic acid (2 equivalents) in toluene. The new compounds have been characterized by MALDI-TOF mass spectrometry and ¹H NMR spectroscopy as well as by several other spectroscopic techniques described subsequently. Although no single-crystal X-ray determination has been carried out in this study for compounds I and II, there is ample precedent for the structures of the new compounds. Furthermore, the structure of the compound, $Mo_2(T^iPB)_2(Bz)_2$, which can be viewed as the parent compound to I is reported below (Fig. 3). We anticipate a planar central phenyl $-CO_2-M_2-CO_2-$



Scheme 1 The synthesis of "bis-bis" model complex M₂(TⁱPB)₂(BMP)₂.



Fig. 3 ORTEP representation of $Mo_2(T^iPB)_2(Bz)_2$ (sea green = molybdenum, scarlet = oxygen, gray = carbon) drawn at 50% probability. Hydrogens, solvent and disorder excluded for clarity.

phenyl unit for all complexes in their ground-state and further that the orientation of the B(mesityl)₂ unit will be such that allows significant B $2p_{\pi}$ -benzoate π conjugation. The mesityl groups, because of their steric influence, will undoubtedly be twisted somewhat out of conjugation with the vacant B $2p_{\pi}$ orbital.

Crystal and molecular structure of Mo₂(TⁱPB)₂(Bz)₂

The benzoate compound, $Mo_2(T^iPB)_2(Bz)_2$, crystallized on a center of inversion located in the middle of the Mo_2 bond. The dihedral angle associated with the CO_2 and the T^iPB moiety is ~96° which effectively removes the ring from conjugation with the metal center. The dihedral angle associated with the CO_2 and the phenyl ring of the benzoate moiety however is less than 9° which allows for considerable conjugation, THF, is coordinated axially along the Mo_2 bond, and the remainder of the structure is similar to M_2 tetracarboxylates previously reported.^{4–7} The structure was, however, significantly disordered and was modeled accordingly. Further refinement details can be found in the ESI[†] and in the Crystallographic Information File (CIF).

Electronic structure calculations

In order to aid in the interpretation of the photophysical properties of the new compounds, we have employed density functional theory DFT and time-dependent DFT as provided by the Gaussian09 program suite. In order to simplify these calculations and save on computational time and resources, we have substituted formate for the bulky T^iPB ligands since in all known structures of the form *trans*- $M_2(T^iPB)_2L_2$ the aryl group of the T^iPB ligands are twisted close to 90° with respect to the carboxylate plane in the aryl rings are not in conjugation with the carboxylate. Thus the approximation or simplification adopted by the model compounds is not so critical. Also in the calculations on the model compounds I' and II' that contain boron we have replaced the mesityl groups by hydrogen atoms with a similar line of reasoning. This assumption was investigated by calculating the simulated UV-Vis spectrum of the molybdenum compound with and without the mesityl substitution. The MLCT band differed by only 3 nm which makes this a reasonable approximation. Similar calculations were performed on the model benzoate complexes *trans*- $Mo_2(O_2CH)_2(O_2CC_6H_5)_2$.

The calculated frontier molecular orbital energy diagram for the molybdenum model complex I' is shown in Fig. 4 along with a comparison for the benzoate complex and a similar diagram for the tungsten complex II' and its benzoate analogue is given in Fig. 5.



Fig. 4 Frontier molecular orbital energy level diagram of model compound I' (right) and the parent benzoate compound $Mo_2(T^iPB)_2(Bz)_2$ (left) (Bz = $O_2CC_6H_5).$



Fig. 5 Frontier molecular orbital energy level diagram of compound II (right) and the parent benzoate compound $W_2(T^{\dagger}PB)_2(Bz)_2$ (left) (Bz = $O_2CC_6H_5$).

The calculations reveal two interesting points. (1) In relation to the benzoates, the introduction of boron as BH₂ in the *para*-position stabilizes the HOMO, the M₂ δ orbital, by ~0.35 eV. (2) The introduction of the BH₂ group greatly lowers the energy of the two ligand based π^* orbitals. Indeed, for molybdenum both the in-phase and out-of-phase L π^* orbitals drop below the Mo₂ δ^* orbital which is predicted to be the LUMO of the benzoate complex.

We also see that the $W_2\delta$ orbital lies higher in energy than its Mo_2 counterpart and that the HOMO–LUMO gap is smaller for the tungsten model compound. Since the HOMO \rightarrow LUMO is a fully allowed electronic transition, a metal to ligand charge transfer, ¹MLCT, we anticipate that the absorption spectrum of the tungsten complex will be red-shifted to its molybdenum counterpart and the ease of electrochemical oxidation will follow in the order II > I.

Electronic absorption and steady state emission spectra

The electronic absorption spectra of the compounds I and II recorded in THF are shown in Fig. 6 along with a comparison with their respective benzoates. As predicted by the electronic structure calculations the MLCT transitions for both complexes are significantly red-shifted in comparison to their benzoate counterparts. The intense broad absorption of the tungsten complex II with its $\lambda_{max} = 755$ nm is entirely consistent with its green colored solutions as is the purple-red color of the molybdenum complex I with $\lambda_{max} = 521$ nm. The tungsten complex II shows an electronic transition at 400 nm which is assignable to the W₂ δ to CO₂ π^* transition associated with the TⁱPB ligands. To higher energy both I and II show bands arising from ligand π to π^* transitions.

The breadth of the ¹MLCT transition in part reflects that an ensemble of rotamers will be present in solution involving various dihedral angles between the O_2C -phenyl-B $2p_{\pi}$ units due to thermal energy which can overcome the thermodynamically favored planar structure. Since the motion of the two *trans* ligands are not correlated, photoexcitation to the MLCT state is likely to be accompanied by a dipole change and we do indeed observe a significant solvent dependence in the ¹MLCT



Fig. 6 Electronic spectra of compounds ${\rm I}$ and ${\rm II}$ with their corresponding parent benzoate compounds in THF.

absorption spectra in toluene and THF (see Fig. S1 in ESI[†]). The steady state emission spectrum shows less of a solvent dependence although compound **I** is only weakly emissive from its S_1 state in toluene. The singlet emission spectrum for compound II regrettably falls too close to the limits of our instrumentation for a reliable comparison.

Both I and II have longer lived triplet states as determined by time-resolved spectroscopy, *vide infra*, but only I shows phosphorescence at 1080 nm which is in relation to the carboxylates of Mo_2^{4+} assignable to emission from the ³MoMo86* state (see Fig. S2 in ESI[†]). Furthermore the lifetime of the T₁ emission is 66 µs (see below) which is notably longer than the lifetimes of ³MLCT states. No phosphorescence is observed for compound II which presumably relaxes by non-radiative decay processes that are favored by the anticipated lower energy of the T₁ state according to the energy gap law.

Electrochemical studies

Both compounds I and II dissolved in THF show a reversible or quasi-reversible oxidation wave in their cyclic voltammograms. These oxidation waves are moved to higher potential relative to their related benzoates. In each case the oxidation potential of the tungsten complex is notably less than that of the molybdenum complex consistent with the calculations that show the $Mo_2\delta$ orbitals to be stabilized relative to their W_2 counterparts.

The compounds I and II also show reduction waves within the solvent window. The reduction wave for the molybdenum complex is quasi-reversible on the time scale of the CV experiment and these reductions correspond to placing an electron in the LUMO which is the in-phase π^* combination of the O₂C-C₆H₄-4-B(mesityl)₂ ligands. From the electrochemical data we can estimate the HOMO–LUMO gap and this is compared with that calculated from the UV-Vis spectra in Table 1.

Time-resolved spectroscopic studies

The excited state of both compounds I and II have been examined by femtosecond transient absorption (fs-TA) spectroscopy which has allowed us to determine the lifetime of the singlet state for the molybdenum complex as 12 and 13 ps in THF and toluene, respectively.

For compound I, we also see a feature at 615 nm in toluene and 650 nm in THF that corresponds to the singlet stimulated emission and has a lifetime of 13 ps in toluene. The red shift of this feature in going from toluene to THF supports the solvent dependence observed in the steady state emission spectra. The singlet excited state, however, is solvent

 Table 1
 The HOMO-LUMO energy gap obtained from the electrochemical experiments and UV-Visible spectra of compounds I and II are compared

Compound	$E_{1/2}(OX)^a$	$E_{1/2}(\text{RED})^a$	$E_{\rm gap}{}^a$	UV-Vis ^b
I	$\begin{array}{c} 0.58 \\ -0.48 \end{array}$	-1.86	2.44	2.35
II		-2.24	1.76	1.63

^{*a*} Volts; $E_{1/2}$ values are referenced to the Cp₂Fe^{+/0} couple. ^{*b*} eV.

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Fig. 7 fs-TA spectrum of I in THF at RT, $\lambda_{ex} = 568$ nm.

independent. The ground state bleach remains at long times indicating the formation of a triplet state. The lifetime was found to be 65.9 μ s by nanosecond transient absorption spectroscopy. These spectral features are shown in Fig. 7 and S9.[†]

Unfortunately for the tungsten complex, the transient signals for the singlet and triplet states lie very close to each other making the kinetics difficult to discern. The peak at 565 nm is attributable to the singlet excited state and has a lifetime of 15 ps. The isosbestic point at 435 nm indicates the formation of a triplet excited state. The lifetime was found to be 75.3 ns by nanosecond transient absorption spectroscopy. These spectra are shown in the ESI.[†]

The influence of fluoride ions

As noted earlier, arylboron compounds have been extensively used in the detection of F⁻ which has a high affinity for coordination to the 3-coordinate boron center. In the present case a THF solution of the molybdenum compound I was titrated with equivalents of $[Bu_4N^+][F^-]$ in THF solution. As shown in Fig. 8, the intense MLCT absorption at 521 nm is completely bleached as the B 2p π -acceptor attached to the benzoate ligand is converted to the $-C_6H_4$ -B(mesityl)₂F⁻ anion. The weak absorption at 400 nm corresponds to the new Mo₂ δ to $-O_2C-C_6H_4$ - transition.

Upon addition of water the F^- anion becomes solvated as can be seen in the spectra shown in Fig. 9 which show the restoration of the MLCT band at 520 nm. The full intensity of this



Fig. 8 Absorption spectrum of I in THF titrated with fluoride ion.



Fig. 9 The absorption spectrum of I in THF first quenched by the addition of fluoride ion and then regenerated by the addition of water.

transition is not restored because the solution has been diluted.

The influence of added F^- on the MLCT of the tungsten complex II is similar and is shown in Fig. S13 in ESI.[†] However, addition of water does not restore the original MLCT and the compound appears to be decomposed in water with time.

Conclusions

The new compounds I and II show intense MLCT bands in the visible region of the spectrum which are notably red shifted compared to the related *trans*- $M_2(T^iPB)_2(O_2CC_6H_5)_2$ due to the influence of the introduction of the B $2p_{\pi}$ acceptor orbital of the B(mesityl)₂ groups. The influence of the vacant $2p_{\pi}$ B orbital is also seen in the calculations on the model compounds. The introduction of F^- ions quenches this intense MLCT absorption in a striking manner in THF solutions. For compound I the addition of water allows the solvation of fluoride and the compound is regenerated as evident by the restoration of the original MLCT.

Experimental section

All reactions and subsequent manipulations of the compounds were performed under one atmosphere of oxygen-free UHPgrade argon using standard Schlenk techniques or in a glove box with a dry and oxygen-free nitrogen atmosphere using standard techniques. Prior to use, all solvents were dried appropriately, distilled, degassed, and stored in flasks equipped with Kontes taps over activated 4 Å molecular sieves under an argon atmosphere. All chemicals were used as received. The starting materials, $M_2(T^iPB)_4$; M = Mo, W, were first prepared according to established procedures.^{8,9} ¹H NMR, MALDI-TOF, and UV-vis data for the compounds are provided below.

NMR

NMR spectra were recorded on a 400 MHz Bruker DPX Advance 400 spectrometer. All ¹H NMR chemical shifts are in ppm relative to the protio impurity in THF- d_8 at 1.73 ppm.

Electronic absorption spectra

Steady-state photophysical measurements were carried out with $10.0 \times 10.0 \text{ mm}^2$ quartz cuvettes equipped with Kontes stopcocks. Electronic absorption spectra at room temperature were recorded using a Perkin-Elmer Lambda 900 spectrometer in THF solution.

Femtosecond transient absorption (TA) experiments were performed using laser and detection systems described previously.¹⁰ Samples were prepared with absorbance ~0.3–0.8 at the excitation wavelengths, which were 568 nm for I in THF, 514 nm for I in toluene, and 800 nm for II in THF. Excitation power at the sample was ~1–2 μ J. The sample for II was kept in constant motion during the experiment by manual movement of an *XYZ* stage to prevent photodecomposition. The TA measurements at a series of pump-probe delay times were performed three times to ensure reproducibility of the results. Spectra collected underwent wavelength calibration and GVD corrections.

Nanosecond TA was performed on compounds I and II in 1 × 1 cm square quartz cuvettes with Kontes stopcocks. Measurements were made on a home-built instrument pumped by a frequency doubled for I (532 nm) or tripled for II (355 nm) Spectra-Physics GCR-150 Nd:YAG laser (fwhm ~8 ns, ~5 mJ per pulse). Signal from a Hamamatsu R928 photomultiplier tube was processed with a Tektronics 400 MHz oscilloscope (TDS 380).¹¹

In general, kinetics were fit to a sum of exponential decay terms, $S(t) = \sum_i A_i \exp(-1/\tau_i) + C$ using Igor Pro 6.0 or SigmaPlot 12.0, where A_i is the amplitude, τ is the lifetime, and *C* is an offset. Error bars for the lifetimes are reported as standard errors of the exponential fits.

Emission spectra

Fluorescence measurements were made on a SPEX Fluoromax-2 spectrofluorimeter in the UV-visible region. Emission measurements in the near-infrared region were performed in J. Young NMR tubes at room temperature and 77 K in 2-methyl THF. Spectra were recorded on a home-built instrument equipped with a germanium detector. All complexes were excited at 405 nm with a RG830 long pass filter between sample and detector.

Electrochemical studies

Cyclic voltammograms were collected at a scan rate of 100 mV s⁻¹ using a Pine Research Instrumentation Wavenow potentiostat-galvanostat. The measurements were performed under a nitrogen atmosphere in a 0.1 M solution of ${}^{n}Bu_{4}NPF_{6}$ in THF using platinum working and platinum auxiliary electrodes patterned on ceramic, with a silver wire pseudo reference electrode (Pine Research Instrumentation). The potentials for all complexes are referenced to the Cp₂Fe/Cp₂Fe⁺ couple.

Mass spectrometry

MALDI-TOF was performed on a Bruker Reflex III mass spectrometer operated in a reflective, positive ion mode with

an N_2 laser. The matrix was prepared as a concentrated solution of dithranol in THF. A small amount of the samples were dissolved in the matrix solution, then spotted onto a MALDI plate with a pipette and allowed to dry.

Electronic structure calculations

The model complexes were optimized in the gas-phase using density functional theory (DFT) utilizing the Gaussian09 suite of programs.^{12,13} The B3LYP functional was used in conjunction with the SDD energy consistent pseudopotentials for molybdenum and tungsten and the 6-31G* basis set for H, C, B, S and O atoms.^{14,15} Vibrational frequency analysis was used to confirm that the optimized structures were minima on the potential energy surface. GaussView plots are shown with an isovalue of 0.02.¹⁶ Electronic absorption spectra were calculated using the time dependent DFT (TD-DFT) method.

Crystallographic information

Single crystals of $Mo_2(T^{i}PB)_2(Bz)_2$ were isolated as bright vellow crystals and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo Ka 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.¹⁷ The structures were solved by the direct methods program in SHELXS-13.18 Full-matrix least-squares refinements based on F^2 were performed in SHELXL-13,18 as incorporated in the WinGX package.19 For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5U_{eq}$ (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2U_{eq}$ (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.20

The crystal was largely disordered, particularly in the TⁱPB moiety which was modeled in two locations and restrained using the SAME, EXYZ and EADP commands. The same procedure was invoked in the disordered solvent THF which was coordinated axially along the Mo_2 bond. Furthermore, it was necessary for the anisotropic U values of this disordered solvent to be restrained using the SIMU command.

CCDC 943288 contains the supplementary crystallographic data for this paper.

Syntheses

4-(Dimesitylboranyl)benzoic acid L–H. Synthesis modified from references.²¹ Dibromobenzene (0.472 g, 2.00 mmol) was dried for 2 h under vacuum on a Schlenk line, dissolved in 15 mL THF and cooled to -78 °C followed by a dropwise addition of *n*-butyl lithium (2.3 M, 0.87 mL, 2.00 mmol) in hexanes. Solution was allowed to stir for 30 min (turned yellow) then a solution of dimesityl boron fluoride (0.536 g, 2.00 mmol) in 20 mL Et₂O was then added slowly to the reaction flask. The flask was kept at -78 °C for 2 h then allowed to reach room temperature overnight. The solvent was removed under vacuum and 4-(bromophenyl)dimesitylborane was obtained as a white powder by column chromatography with hexanes as eluent. Yield: 0.567 g (70%). ¹H NMR (CDCl₃): $\delta_{\rm H}$ (250 MHz) 7.49 (d, 2H, $J_{\rm HH}$ = 8 Hz), 7.36 (d, 2H, $J_{\rm HH}$ = 8 Hz), 6.82 (s, 4H), 2.31 (s, 6H), 1.99 (s, 12H) ppm.

4-(Bromophenyl)dimesitylborane (0.500 g, 1.23 mmol) was dried for 2 h under vacuum on a Schlenk line, dissolved in 20 mL THF and cooled to -78 °C followed by a dropwise addition of *n*-butyl lithium (2.5 M, 0.49 mL, 1.23 mmol) in hexanes. Solution was allowed to stir for 30 min (turned red) then carbon dioxide was passed through a drying tube filled with anhydrous calcium sulfate and bubbled through the reaction solution for 2 h (turned cloudy white). The flask was opened to air and the product was extracted with dichloromethane after acid workup followed by a recrystallization with hexanes to give a white powder. Yield: 0.310 g (67%). ¹H NMR (CDCl₃): $\delta_{\rm H}$ (250 MHz) 8.05 (d, 2H, $J_{\rm HH}$ = 8 Hz), 7.59 (d, 2H, $J_{\rm HH}$ = 8 Hz), 6.83 (s, 4H), 2.32 (s, 6H), 1.98 (s, 12H) ppm.

 $Mo_2(T^{i}PB)_2L_2$ (I) L–H (0.070 g, 0.189 mmol) and $Mo_2(T^{i}PB)_4$ (0.112 g, 0.095 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a red solution. The solvent was removed *in vacuo* and the resulting orange solid was washed 3 times with 20 mL of hexanes and dried. (Yield: 65%) ¹H NMR (THF d_8): δ_H (400 MHz) 8.36 (d, 4H, J_{HH} = 8 Hz), 7.68 (d, 4H, J_{HH} = 8 Hz), 7.00 (s, 4H), 6.86 (s, 8H), 3.03 (m, 2H), 2.88 (m, 4H), 2.30 (s, 12H), 2.08 (s, 24H), 1.24 (d, 12H, J_{HH} = 7 Hz), 1.04 (d, 24H, J_{HH} = 7 Hz) ppm. UV-Vis: (in THF at 293 K) 521 nm, 322 nm; (in toluene at 293 K) 488 nm, 323 nm; (in pyridine at 293 K) 541 nm, 440 nm. MALDI-TOF: Calculated: 1432.6. Found: 1432.3 (M⁺).

W₂(**T**ⁱ**PB**)₂**L**₂ (**II**) L–H (0.080 g, 0.216 mmol) and W₂(**T**ⁱ**PB**)₄ (0.147 g, 0.108 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a blue solution. The solvent was removed *in vacuo* and the resulting blue solid was washed 3 times with 20 mL of hexanes and dried. (Yield: 55%) ¹H NMR (THF-*d*₈): $\delta_{\rm H}$ (400 MHz) 8.13 (d, 4H, $J_{\rm HH}$ = 8 Hz), 7.66 (d, 4H, $J_{\rm HH}$ = 8 Hz), 6.99 (s, 4H), 6.86 (s, 8H), 3.01 (m, 2H), 2.83 (m, 4H), 2.30 (s, 12H), 2.07 (s, 24H), 1.23 (d, 12H, $J_{\rm HH}$ = 7 Hz), 0.99 (d, 24H, $J_{\rm HH}$ = 7 Hz) ppm. UV-Vis: (in THF at 293 K) 754 nm, 402 nm, 322 nm. MALDI-TOF: Calculated: 1604.7. Found: 1604.0 (M⁺).

 $Mo_2(T^iPB)_2(Bz)_2$ Bz-H (0.041 g, 0.339 mmol) and $Mo_2(T^iPB)_4$ (0.208 g, 0.177 mmol) were dissolved in toluene and allowed to stir for 3 days yielding an yellow solution. The solvent was removed *in vacuo* and the resulting yellow solid was washed 3 times with 20 mL of hexanes and dried. (Yield: 40%) ¹H NMR (THF- d_8): δ_H (400 MHz) 8.38 (d, 4H, J_{HH} = 6 Hz), 7.56 (d, 4H, J_{HH} = 6 Hz), 6.99 (s, 4H), 3.03 (m, 2H), 2.87 (m, 4H), 1.23 (d, 12H, J_{HH} = 7 Hz), 1.02 (d, 24H, J_{HH} = 7 Hz) ppm. UV-Vis: (in THF at 293 K) 429 nm, 339 nm. MALDI-TOF: Calculated: 932.2. Found: 932.7 (M⁺).

 $W_2(T^iPB)_2(Bz)_2$ Bz-H (0.041 g, 0.399 mmol) and $W_2(T^iPB)_4$ (0.230 g, 0.169 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a red solution. The solvent was removed *in vacuo* and the resulting red solid was washed 3 times with 20 mL of hexanes and dried. (Yield: 35%) ¹H NMR (THF- d_8):

 $\delta_{\rm H}$ (400 MHz) 8.16 (d, 4H, $J_{\rm HH}$ = 8 Hz), 7.71 (d, 4H, $J_{\rm HH}$ = 8 Hz), 6.98 (s, 4H), 3.01 (m, 2H), 2.84 (m, 4H), 1.22 (d, 12H, $J_{\rm HH}$ = 7 Hz), 0.96 (d, 24H, $J_{\rm HH}$ = 7 Hz) ppm. UV-Vis: (in THF at 293 K) 593 nm, 557 nm, 405 nm. MALDI-TOF: Calculated: 1108.3. Found: 1107.8 (M⁺).

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Notes and references

- 1 C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574–4585.
- 2 Y. Sun and S. Wang, Inorg. Chem., 2009, 48, 3755-3767.
- 3 C. R. Wade and F. P. Gabbaï, *Inorg. Chem.*, 2010, **49**, 714–720.
- 4 B. G. Alberding, M. H. Chisholm, J. C. Gallucci, Y. Ghosh and T. L. Gustafson, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 8152–8156.
- 5 S. E. Brown-Xu, M. H. Chisholm, C. B. Durr, S. A. Lewis, V. Naseri and T. F. Spilker, *Chem. Sci.*, 2013, 4, 2105–2116.
- G. T. Burdzinski, M. H. Chisholm, P.-T. Chou, Y.-H. Chou,
 F. Feil, J. C. Gallucci, Y. Ghosh, T. L. Gustafson, M.-L. Ho,
 Y. Liu, R. Ramnauth and C. Turro, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 15247–15252.
- 7 M. H. Chisholm and B. J. Lear, *Chem. Soc. Rev.*, 2011, 40, 5254–5265.

- 8 F. A. Cotton, L. M. Daniels, E. A. Hillard and C. A. Murillo, *Inorg. Chem.*, 2002, 41, 1639–1644.
- 9 B. G. Alberding, M. H. Chisholm, Y.-H. Chou, J. C. Gallucci, Y. Ghosh, T. L. Gustafson, N. J. Patmore, C. R. Reed and C. Turro, *Inorg. Chem.*, 2009, 48, 4394–4399.
- 10 G. Burdzinski, J. C. Hackett, J. Wang, T. L. Gustafson, C. M. Hadad and M. S. Platz, *J. Am. Chem. Soc.*, 2006, **128**, 13402–13411.
- 11 M. J. Byrnes, M. H. Chisholm, J. A. Gallucci, Y. Liu, R. Ramnauth and C. Turro, J. Am. Chem. Soc., 2005, 127, 17343–17352.
- 12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, *et al.*, *GAUSSIAN 09*, Gaussian, Inc., Wallingford, CT, 2003.
- 13 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- 14 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **137**, A1697–A1705.
- 15 A. D. Becke, Phys. Rev., 1988, 38, 3098-3100.
- 16 R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell and R. Gilliland, *GaussView 5.0*, Semichem Inc., Shawnee Mission, KS, 2003.
- 17 Z. Otwinowski and W. Minor, *Methods in Enzymology*, *Vol. 276: Macromolecular Crystallography, Part A*, Academic Press, 1997.
- 18 G. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112–122.
- 19 L. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.
- 20 A. J. C. Wilson and V. Geist, *International Tables for Crystallography, Volume C*, Kluwer Academic Publishers, Dordrecht, 1992.
- 21 W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao and S. Wang, *Chem.-Eur. J.*, 2004, **10**, 994–1006.