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Electronic communication within flexible bisdithiolene ligands bridging molybdenum centers.

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Abstract

Bimetallic molybdenum dithiolene complexes involving two flexible ditopic conjugated linkers have been synthesized and characterized by electrochemistry, spectro-electrochemistry and single crystal X-ray diffraction. The electrochemical investigations evidence that the two metallic bisdithiolene moieties are electronically coupled in the monocationic state. DFT and TD-DFT calculations further suggest that the intervalence charge transfer within both monocations is essentially localized on the ligand and can be described as an intra-ligand charge transfer (ILCT).

Introduction

Electronic communication in bimetallic complexes have attracted a lot of attention both from a theoretical point of view and for potential applications in molecular electronics or as model to

mimic biological electron transfer.^{1,2} These systems are also appealing models to understand electronic conduction within extended networks. Bisdithiolene ligands are interesting as conjugated bridging organic moieties between redox active metal centers as they may potentially mediate or even participate into metal/metal electronic coupling. Indeed dithiolene ligands are considered as archetypical non-innocent ligands, and, thanks to electron delocalization over the metallacycle generated by the mixing of the metal and ligand orbitals, metalladithiolene complexes present multiple and successive addressable redox states.^{3,4} Among the few bisdithiolene ligands reported to date, some are rigid and present both dithiolene units in the same plane such as tetrathiooxalate (tto)⁵ or 1,2,4,5-benzenetetrathiolate (btt)⁶ (Chart 1). Both ligands have led to various bi- or poly-metallic complexes where strong electronic interactions between the redox units have been evidenced.^{5,6,7} Another planar bisdithiolene ligand is tetrathiafulvalene-4,4',5,5'-tetrathiolate (TTFtt, Chart 1). Different bimetallic complexes have been reported but no electronic interaction has been observed between the redox-active metallic centers across the TTF backbone.⁸ The second class of bisdithiolene ligands consists of two dithiolene moieties that are not constrained to coplanarity, such as 1,2,3,4-butadiene tetrathiolate (bdtt),⁹ 4,4'-di(benzenedithiolate) (dbdt, **L1**)¹⁰ or benzene-1,4-di(ethylenedithiolate) (bdedt, **L2**) (Chart 1). It is worth mentioning that for the two latter bisdithiolene ligands, no bimetallic complexes have been reported so far, while only one example of a tetranuclear complex with a close ligand (**Me₃Si**)₂**L2** is described (see Chart 2).¹¹ Considering the scarcity of such complexes, we decided to investigate how these flexible ligands, namely dbdt (**L1**) and bdedt (**L2**), can act as bridging moieties between two metallic centers.

Chart 1

In order to probe the possible electronic communication along or within these organic bridges including the two (metal)dithiolene moieties, we focused our attention on their bis(cyclopentadienyl) dithiolene molybdenum complexes, $\text{Cp}_2\text{Mo}(\text{dithiolene})$. Indeed, these d^2 complexes belong to an interesting family of redox active derivatives that can be easily oxidized reversibly into the cation radical and the dicationic species.^{12,13,14,15,16} Herein, we report the synthesis of two bimetallic complexes, namely $(\text{Cp}_2\text{Mo})_2(\text{dbdt})$ and $(\text{Cp}_2\text{Mo})_2(\text{bdedt})$ (**Mo₂L1** and **Mo₂L2** respectively, Chart 2). Electrochemical and spectroelectrochemical investigations, supported by DFT calculations, evidence that, although potentially flexible, these ligands can give rise to strong electronic interaction between the metalladithiolene units.

Chart 2

Results and discussion

Synthesis of the proligands. Various protecting groups of the dithiolene ligand have been proposed to prepare dithiolene complexes: either organic protecting groups such as cyanoethyl and carbonyl groups¹⁷ or inorganic ones such as dialkyltin¹⁸ and zinc complexes.¹⁹ Deprotection requires the use of a strong base (sodium methanolate) in the case of an organic protecting group. On the other hand, inorganic protecting groups are readily displaced by metal dichloride derivatives by ligand exchange so that no specific deprotecting step is needed. Such a transmetallation realized with dialkyltin protected molecule is known to be cleaner than with zinc and to generate highly soluble by-products that are easier to work up.¹⁸ Therefore, we decided to prepare the target bisdithiolene protected ligands by a dialkyltin group **Sn₂L1** and **Sn₂L2** as shown in Chart 3.

The synthesis of ligand **L1** protected by dimethyltin groups has been reported previously.¹⁰ However, in order to increase the solubility of this proligand, dibutyltin derivative **Sn₂L1** was prepared instead. For the second bridging ligand, **L2**, the dithiole-2-one protected ligand was first prepared, and further converted into the dibutyltin protected **Sn₂L2** (Scheme 1). For that purpose, 1,4-bis(bromoacetyl)benzene **1** was reacted with potassium xanthate salt.²⁰ The ring closure was performed in acidic medium to afford the 4,4'-(1,4-phenylene)bis-1,3-dithiol-2-one **2**. In order to generate the dibutyltin protected dithiolene ligand, we used **2** as starting material. The dithiolene ligand was first deprotected through the use of sodium methanolate and then reacted with dichlorodibutyltin to afford the protected dithiolene ligand **Sn₂L2**. Recrystallization of those two proligands afforded crystals suitable for X-ray diffraction studies. The molecular structure of both proligands **2** and one of the two crystallographically

independent molecule **Sn₂L2** (molecule A) are presented in Figure 1. Selected bond lengths and angles are collected in Table 1. As expected, both proligands **2** and **Sn₂L2** are not planar (Figure 1): in **2**, the dihedral angle between the dithiol-2-one rings and the phenyl ring is 22.8(2)°, while in **Sn₂L2**, the angle between the metalladithiolene moieties and the phenyl rings is 35.4(2)° for molecule A and 33.9(6)° for molecule B. The dithiole dibutyltin heterocyclic rings are themselves distorted along the S...S hinge with an angle of 20.2 (2)° in molecule A and 10.7(9)° in molecule B.

Figure 1 Molecular structures of proligands **2** (top) and **Sn₂L2** (one of two crystallographically independent molecules, molecule A, bottom). Thermal ellipsoids are drawn at 50% probability level. H atoms have been omitted for clarity.

Syntheses of the complexes. The chemical approach followed for the synthesis of the target molecules is described in Scheme 2. The reactivity of the protected bis(phenyldithiolene) ligand **Sn₂L1** towards Cp₂MoCl₂ was first studied. By simply heating a solution of this ligand with an excess of Cp₂MoCl₂ in CHCl₃/THF (50/50) the desired complex **Mo₂L1** was successfully formed in 35 % yield together with the mono molybdenum complex **SnL1Mo** in 15 % yield. **Mo₂L1** and **SnL1Mo** were easily separated by column chromatography. The reaction of the dibutyltin protected proligand **Sn₂L2** with Cp₂MoCl₂ was also attempted. However, whatever the experimental conditions tested it was impossible to isolate the desired complex. Nevertheless, addition of NaOMe to the proligand 4,4'-(1,4-phenylene)bis-1,3-dithiol-2-one **2** followed by the addition of an excess of Cp₂MoCl₂ gave **Mo₂L2** in 85% yield (Scheme 2).

Crystals suitable for X-ray structure analysis were obtained for both **Mo₂L1** and **Mo₂L2**. **Mo₂L1** was isolated as a dichloromethane solvate and **Mo₂L2** as a chloroform solvate formulated respectively as **Mo₂L1**·0.5CH₂Cl₂ and **Mo₂L2**·0.5CHCl₃. These compounds

crystallize in the monoclinic system, space group $P2_1/n$ for **Mo₂L1**.0.5CH₂Cl₂ and $P2_1/c$ for **Mo₂L2**.0.5CHCl₃. The molecular structures of both complexes are presented in Figure 2. Selected bond lengths and angles are listed in Table 1 together with those of the reference compounds Cp₂Mo(bdt) and Cp₂Mo(sdt) (bdt: benzenedithiolate and sdt: styrene-1,2-dithiolate).

Table 1. Bond lengths (Å) and θ angles (°) in the metallacycle for complexes **Sn₂L2**, **Mo₂L1**, **Mo₂L2**, Cp₂Mo(sdt) and Cp₂Mo(bdt)

Cp₂Mo(sdt)

Cp₂Mo(bdt)

	M-S	C-S	C=C	θ
Sn₂L2	Molecule A			
	Sn ₁ -S ₁ 2.419(2)	S ₁ -C ₁ 1.753(6)		
	Sn ₁ -S ₂ 2.436(1)	S ₂ -C ₂ 1.765(5)	1.344(8)	20.2(2)
	Molecule B			
	Sn ₂ -S ₂₁ 2.428(2)	S ₂₁ -C ₂₁ 1.756(9)		
	Sn ₂ -S ₂₂ 2.427(2)	S ₂₂ -C ₂₂ 1.773(5)	1.334(9)	10.7(9)
Mo₂L1	Mo ₁ -S ₁ 2.437(1)	S ₁ -C ₁₁ 1.763(4)	1.406(6)	2.6(2) (Mo ₁)
	Mo ₁ -S ₂ 2.446(1)	S ₂ -C ₁₂ 1.764(4)		
	Mo ₂ -S ₃ 2.434(1)	S ₃ -C ₃₁ 1.755(4)	1.402(6)	5.1(1) (Mo ₂)
	Mo ₂ -S ₄ 2.441(1)	S ₄ -C ₃₂ 1.767(4)		
Cp ₂ Mo(bdt) ²¹	Mo-S 2.437(3)	1.78(1)	1.35(3)	9
Mo₂L2	Mo ₁ -S ₁ 2.438(2)	S ₁ -C ₁₁ 1.766(10)	1.333 (14)	4.2(3) (Mo ₁)
	Mo ₁ -S ₂ 2.438(3)	S ₂ -C ₁₂ 1.735(10)		
	Mo ₂ -S ₁₁ 2.445(2)	S ₁₁ -C ₃₂ 1.769(11)	1.345 (14)	3.1(3) (Mo ₂)
	Mo ₂ -S ₁₂ 2.438(3)	S ₁₂ -C ₃₁ 1.727(10)		
Cp ₂ Mo(sdt) ²²	Mo ₁ -S ₁ 2.4402(7)	S-C 1.771(3)	1.327(3)	planar
	Mo ₁ -S ₂ 2.4396(7)	S-C 1.746(3)		

For both complexes, the MoS₂C₂ metallacycles are nearly planar with a folding angle θ , along the S...S hinge of the metallacycle, in the range of 2.6-5.1°, in line with the corresponding values obtained Cp₂Mo(bdt)²¹ and Cp₂Mo(sdt).²² The bond lengths and bond angles of the metallacycles are also in the range of those found for the monometallic references compounds.^{21,22} (Table 1). In both complexes the organic spacers are not planar. Indeed, in **Mo₂L1** a dihedral angle of 41.9(1)° is observed between the two phenyl rings and in **Mo₂L2** the two dihedral angles between the C₂S₂ planes and the phenyl ring reach 28.9(3)° (Mo₁) and 26.7(3)° (Mo₂).

Figure 2 Molecular structures of the two complexes, **Mo₂L1** (top) and **Mo₂L2** (bottom). Thermal ellipsoids are drawn at 50% probability level. H atoms have been omitted for clarity.

Electrochemical investigations. The redox properties of **SnL1Mo**, **Mo₂L1** and **Mo₂L2** were evaluated by cyclic voltammetry (CV) performed in CH₂Cl₂ in the presence of 0.1 M of NBu₄PF₆ as supporting electrolyte. CVs are reported in Figure 3 while the deduced half-wave redox potentials are summarized in Table 2. Cp₂Mo(dithiolene) complexes are known to be reversibly oxidized into a cation radical and a dicationic species. Considering the

monosubstituted Cp_2Mo biphenyl **SnL1Mo**, the CV indeed displays two reversible monoelectronic oxidation waves. As the oxidation of **Sn₂L1** occurs at a higher potential, 1.1 V vs SCE, (see SI), the two redox processes are attributed to the oxidation of the $\text{Cp}_2\text{Mo}(\text{dithiolene})$ moiety into the radical cation and dicationic species. (Figure 3A, red CV). For the complexes with two $\text{Cp}_2\text{Mo}(\text{dithiolene})$ units, two types of behavior can be envisioned. If the two $\text{Cp}_2\text{Mo}(\text{dithiolene})$ moieties of each complex behave independently, both electrophores should be oxidized at the same potential leading to only two redox waves on the CV. Contrariwise, if electronic interactions occur between the two metalladithiolene units, then the oxidation of those moieties should occur separately at different potentials leading to multi redox processes.

Figure 3. Cyclic voltammograms and Differential Pulse Voltammetry (DPV, top) of **Mo₂L1** (A, black), **Mo₂L2** (B) and cyclic voltammogram **SnL1Mo** (A, red) in CH_2Cl_2 - Bu_4NPF_6 0.1 M (100 mV/s).

Here, for both bimetallic complexes **Mo₂L1** and **Mo₂L2**, the CVs display multi redox processes suggesting a sizeable electronic interaction between the two $\text{Cp}_2\text{Mo}(\text{dithiolene})$ moieties

through the organic linker. In both cases, the first two processes are fully reversible ($E_1 = 0.25$ V and $E_2 = 0.37$ V vs. SCE for **Mo₂L1** ; $E_1 = 0.03$ V and $E_2 = 0.19$ V vs. SCE for **Mo₂L2**) as shown in Figure 3. This indicates the stepwise oxidation of each neutral Cp₂Mo(dithiolene) moiety into the radical cation. The other oxidation processes occur at a more anodic potential and the shape of these broad waves indicates the adsorption of an oxidized species on the electrode followed by a sharp desorption reduction peak. Thus, the CVs of the two bimetallic complexes **Mo₂L1** and **Mo₂L2** show two well defined redox processes followed by a third and broad one involving adsorption at the electrode. This is also confirmed by Differential Pulse Voltammetry (DPV) (Inserts in Figure 3). The redox potentials and the potential difference between the redox processes vary significantly between these two complexes which were analyzed in the same conditions (Table 2). Due to the presence of the two electron rich Cp₂Mo(dithiolene) moieties, the first redox process of the bimetallic complex **Mo₂L1** occurs at a less anodic potential than that of the monosubstituted one **SnL1Mo** ($E_1 = 0.25$ V for **Mo₂L1** and $E_1 = 0.34$ V vs. SCE for **SnL1Mo**). In addition, comparison between the two bimetallic complexes highlights the effect of the fusion between the phenyl ring and the Cp₂Mo(dithiolene) moiety as there is an anodic shift of about 220 mV of the first anodic process for **Mo₂L1** ($E_1 = 0.25$ V vs. SCE) compared to **Mo₂L2** ($E_1 = 0.03$ V vs. SCE). Concerning the potential difference between the first two redox processes ($\Delta E_{1/2} = E_{1/2}^2 - E_{1/2}^1$), it amounts to 120 mV for **Mo₂L1** while $\Delta E_{1/2}$ reaches 160 mV for **Mo₂L2**. This result is in stark contrast with that obtained for the tetrametallic Mo complex (shown in Chart 1)¹¹ where no electronic interaction along the bridging ligand ((**Me₃Si**)₂**L2**) was detected by cyclic voltammetry. The $\Delta E_{1/2}$ values measured in the same conditions (CH₂Cl₂-Bu₄NPF₆ 0.1 M) can be compared²³ and correspond to comproportionation constants, K_c , in the same range for both complexes namely 1×10^2 and 5×10^2 for **Mo₂L1** and **Mo₂L2** respectively. Charge transfer in mixed valence molecules is often considered to depend on the distances between both redox active sites.²⁴

Here, the intramolecular Mo-Mo distance reaches 12.75 Å and 12.32 Å for **Mo₂L1** and **Mo₂L2** respectively. These very close distances are in accordance with the slight difference obtained in the respective *K_c* values. These values are nevertheless much lower than those found for some bimetallic complexes⁶ of the benzenetetrathiolate (btt) ligand which exhibit much shorter M-M distances (~8.45 Å) (e.g. *K_c* = 1.6 10¹¹ also determined in CH₂Cl₂-Bu₄NPF₆ 0.1 M for compound 3d in reference 6c).

Table 2. Half-wave redox potentials^a of complexes, **SnL1Mo**, **Mo₂L1** and **Mo₂L2** in CH₂Cl₂ (E in V vs SCE).

Compound	E _{1/2} ¹ (ΔE _p) ^b	E _{1/2} ² (ΔE _p)	E _{pa} /E _{pc} ³ (ΔE _p)
SnL1Mo	0.34 (60)	0.97 (60)	
Mo₂L1	0.25 (60)	0.37 (60)	1.07/0.97 (100)
Mo₂L2	0.03 (60)	0.19 (60)	0.95/0.88 (70)
Cp ₂ Mo(sdt) ^{c,22}	0.34	-	-

^a oxidation processes, taken as the average of the anodic and the cathodic peak potentials. ^b ΔE_p (in mV) : peak-to-peak separation. ^c Analysed in DMF.

Spectroelectrochemical studies. UV-vis-NIR spectroelectrochemical investigations were performed on dichloromethane solution of the three **SnL1Mo**, **Mo₂L1** and **Mo₂L2**. These three neutral complexes exhibit absorption bands in the UV-vis range only. The lowest energy band in these neutral complexes is assigned to a ligand-metal charge transfer (LMCT) band from dithiolene to Mo.²⁵ The LMCT nature of the low energy absorption band has been confirmed with TD-DFT calculations on **Mo₂L1** and **Mo₂L2** (see supporting information). Gradual oxidation of the monosubstituted complex **SnL1Mo** to the monocation radical species

leads to the growth of new absorption bands centered at 670 nm and 1140 nm, as typically observed with $\text{Cp}_2\text{Mo}(\text{dithiolene})$ complexes.^{22,26}

Figure 4 UV-vis-NIR absorption spectra of complex **SnL1Mo** monitored from the neutral state to the monocation radical state upon electrochemical oxidation.

The spectra recorded upon oxidation from the neutral to the monocationic state of the bimetallic complexes **Mo₂L1** and **Mo₂L2** show different features. Indeed, the gradual oxidation of **Mo₂L1** to the monocationic species leads to the growth of new absorption bands in the visible region at 476 and 702 nm together with the appearance of a weak absorption at 998 nm and a broader one centered at 1596 nm in the NIR region (Figure 5), the latter being ascribed to the signature of a mixed valence species. Continued gradual oxidation to the bis(cationic) species induces the decrease of the bands observed in the NIR together with the appearance of a new absorption band centered at 1170 nm. It is interesting to compare the evolution of the absorption spectra of **Mo₂L1** upon gradual oxidation with those of complex **SnL1Mo** where only one Mo atom is connected to a dithiolene group. The signature of the single cation radical species in **SnL1Mo** (Figure 4) is similar to that observed for the biscationic species in **Mo₂L1** (Figure 5, right) suggesting close electronic structures. DFT calculations on **Mo₂L1**²⁺ show that the triplet state is more stable by 0.25 eV compared to the singlet state so that **Mo₂L1**²⁺ can be consistently described as a dication diradical.

Figure 5 UV-vis-NIR absorption spectra monitored from the neutral state to the monocationic state (left) and from the monocationic state to the bicationic state (right) upon electrochemical oxidation of **Mo₂L1**.

Investigations carried out on **Mo₂L2** show similar trends (Figure 6). Gradual oxidation to the monocation radical species of **Mo₂L2** leads to the growth of new absorption bands centered at 534 and 632 nm together with a broad one in the NIR region. The latter is again ascribed to the formation of a mixed valence species. This band can tentatively be deconvoluted into two bands centered at 1732 nm and 2493 nm. Then, upon oxidation to the bicationic species, the intensity of these bands observed in the NIR region vanish gradually giving way to the emergence of two new bands centered at 870 and 1154 nm. An isosbestic point at 1318 nm evidences the co-existence of the two different species in the medium (cation radical and dication diradical). There again the spectrum of the bis oxidized species of **Mo₂L2** shows some close similarities with that of the cation radical species of **SnMoL1**.

Figure 6 UV-vis-NIR absorption spectra monitored from the neutral state to the monocationic state (left) from the monocationic state to the bicationic state (right) upon electrochemical oxidation of **Mo₂L₂**.

Thus, the band observed at lower energy upon the gradual oxidation of **Mo₂L₁** and **Mo₂L₂** to the monooxidized species can be viewed as an intervalence charge-transfer (IVCT), in line with the CV analysis. To further characterize this electronic communication between the two $\text{Cp}_2\text{Mo}(\text{dithiolene})$ moieties along the organic bridge DFT and TD-DFT calculations were carried out on these two bimetallic complexes.

DFT and TD-DFT calculations. Geometry optimizations carried out on **Mo₂L₁** and **Mo₂L₂** in the neutral state [Gaussian03, B3LYP/LanL2DZ] lead to a slightly folded MoS_2C_2 metallacycle and a HOMO delocalized over the whole organic spacer with little metal contribution (Figure 7). The agreement of the experimental and calculated bond lengths for the neutral species is reasonably good (calculated bond distances and angles are reported in Tables S1 and S2 in the supporting information). The LUMO of both complexes are centered essentially on the molybdenocene moiety at near identical energy level (ca. -2 eV). The calculated energy level for the HOMO in **Mo₂L₂** (-4.27 eV) is notably higher in energy by 0.22

eV than that of the HOMO in **Mo₂L1** (-4.49 eV) in perfect accordance with the relative redox potentials differing by 220 mV determined by cyclic voltammetry (0.03 V vs. 0.25 V respectively, *vide supra*).

Figure 7 Frontier molecular orbitals (HOMO and LUMO) and calculated energy levels for complexes **Mo₂L1** (left) and **Mo₂L2** (right) shown with a cutoff of 0.04 [e/bohr³]^{1/2}.

In the radical cation state as well as in the bis(oxidized) one, both complexes exhibit a planarization of the MoS₂C₂ metallacycle and a SOMO delocalized on the bisdithiolene organic spacer with no or very little contribution of the metal (Figure 8). Moreover, upon oxidation to the monocation, for both complexes a planarization of the organic spacers is observed with reduced dihedral angles either between the two phenyl rings by 8° in **Mo₂L1** or between the C₂S₂ planes and the phenyl ring by 7° in **Mo₂L2** (see SI). Interestingly, in these optimized structures the bond lengths evolution of the dithiolene moieties shows a decrease of the C-S distances together with an increase of the C-C bond lengths (Table S1 and S2). These observations are in excellent agreement with a primarily ligand based electron transfer.

Figure 8 Frontier molecular orbitals (SOMO and LUMO) of the monooxidized species and calculated energy levels for complexes **Mo₂L1** (left) and **Mo₂L2** (right) shown with a cutoff of 0.04 [e/bohr³]^{1/2}.

TD-DFT calculations on optimized geometry of the doublet state of monocationic **Mo₂L1** and **Mo₂L2** identify an intense and broad low energy transition with a significant oscillator strength. For both monocationic complexes the major contribution in this low energy transition arises from the frontier spin orbitals, both essentially delocalized over the bridging ligand and with negligible contribution from the metallocene moieties. This is consistent with the assignment of this band as being an IVCT from spectroelectrochemical investigations (*vide supra*). For both cations of **Mo₂L1** and **Mo₂L2** the IVCT is proposed to be ligand centered (intra-ligand charge transfer) with the metallocene moieties playing the role of ‘anchors’ and electron donors for the non-innocent bisdithiolene bridging ligand.^{3,4}

Conclusion

Bimetallic complexes involving biscyclopentadienyl Mo(dithiolene) moieties namely (Cp₂Mo)₂(dbdt) and (Cp₂Mo)₂(bdedt) (**Mo₂L1** and **Mo₂L2** respectively) have been synthesized. The Cp₂Mo(dithiolene) fragment was selected for its well-known and easily accessible redox

activity and the two organic linkers for their possible structural flexibility despite their conjugated skeleton. Two types of proligands have been evaluated: either the bisdithiolene protected by a carbonyl group or by a dialkyltin one. Transmetallation of the dialkyltin group in **Sn₂L1** in the presence of Cp₂MoCl₂ afforded the desired **Mo₂L1** complex whereas it turned out that with the second protected ligand **Sn₂L2** no bimetallic complex was obtained. However, **Mo₂L2** was successfully prepared through the use of the dithiole-2-one pro-ligand. Electrochemical and UV-vis-NIR spectroelectrochemical investigations have evidenced electronic interactions between the two organometallic electrophores along the organic linker. This can be detected electrochemically by the sequential oxidation of each Cp₂Mo(dithiolene) moiety with a $\Delta E_{1/2}$ value of 120 and 160 mV. The recorded spectra of the monocharged species evidenced a broad absorption band assigned to an intervalence charge transfer band (IVCT). DFT calculations suggest that this IVCT can be better described as an essentially bridging ligand-based process assisted by the electron rich metallocene moieties anchored to the linker through the non-innocent bisdithiolene fragments.

Experimental section

General. NMR spectra were recorded at room temperature using CDCl₃ unless otherwise noted. Chemical shifts are reported in ppm and ¹H NMR spectra were referenced to residual CHCl₃ (7.26 ppm) and ¹³C NMR spectra were referenced to CHCl₃ (77.2 ppm). Mass spectra were recorded with Agilent 6510 instrument for organics compounds, and with Thermo-Fisher Q-Exactive instrument for complexes by the Center Régional de Mesures Physiques de l'Ouest, Rennes. CVs were carried out on a 10⁻³ M solution of complex in CH₂Cl₂-[NBu₄][PF₆] 0.1 M. CVs were recorded on a Biologic SP-50 instruments at 0.1 Vs⁻¹ on a platinum disk electrode. Potentials were measured *versus* KCl Saturated Calomel Electrode (SCE). The spectroelectrochemical setup was performed in CH₂Cl₂-[NBu₄][PF₆] 0.2 M using a Pt grid as

the working electrode, a Pt wire as the counter electrode and SCE reference electrode. A Shimadzu 3600 plus spectrophotometer was employed to record the UV-vis-NIR spectra. Column chromatography was performed using silica gel Merck 60 (70-260 mesh). All reagents and materials from commercial sources were used without further purification. The complexes were synthesized under an argon atmosphere using standard Schlenk techniques. The solvents were purified and dried by standard methods. Compound **2** was synthesized according to literature procedure.¹⁰

Synthesis of 4,4'-(1,4-phenylene)bis-1,3-dithiol-2-one **2.** To a solution of 1,4-bis(bromoacetyl)benzene **1** (4.00 g, 12.5 mmol) in 150 mL of dichloromethane was added potassium isopropylxanthate (4.35 g, 25.0 mmol). The mixture was stirred for one hour, and the precipitate of KBr that formed was separated by filtration through Celite and washed with CH₂Cl₂ (100 mL). The combined washing and filtrate were then taken to dryness under reduced pressure to afford the xanthate ester as a bright yellow solid (5.37 g), which was used without further purification. Mp = 136°C; ¹H NMR (300 MHz) δ 1.37 (d, 12H, ³J = 6.2 Hz, CH₃), 4.64 (s, 4H, CH₂), 5.70 (hept, 2H, ³J = 6.2 Hz, CH(CH₃)₂), 8.12 (s, 4H, Ar); ¹³C NMR ((CD₃)₂SO, 101 MHz, T = 383 K) δ 21.3 (CH₃), 43.3 (CH₂), 79.3 (CH(CH₃)₂), 128.9 (4Ar), 139.5 (2Ar), 192.1 (C=O), 212.1 (C=S); HRMS (ESI) calcd for C₁₈H₂₂O₄NaS₄ [M+Na]⁺: 453.02932. Found: 453.0295. To 100 mL of concentrated sulfuric acid was slowly dropped at 0°C the xanthate ester (5.37 g, 12.5 mmol). The solution was stirred 6 hours at 0°C and poured in 800 mL of iced water. The precipitate was filtered off and washed with water and ethanol. The precipitate was dried overnight in oven to afford 4,4'-(1,4-phenylene)bis-1,3-dithiol-2-one **2** (3.13 g, 10.1 mmol) as light beige solid. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of a toluene solution. Yield: 81%; Mp = 214°C; ¹H NMR ((CD₃)₂SO, 300 MHz) δ 7.65 (s, 4H, Ar), 7.76 (s, 2H, =CH); ¹³C NMR ((CD₃)₂SO, 100 MHz) 114.7 (SCH=C), 126.4 (4Ar), 131.8 (2Ar), 132.1 (SC=CH), 191.1 (C=O); HRMS (ESI) calcd for C₁₂H₆O₂NaS₄

[M+Na]⁺: 332.91484. Found: 332.9142; Anal calcd for C₁₂H₆O₂S₄: C, 46.43; H, 1.95; S, 41.31. Found: C, 46.18; H, 1.83; S, 40.77.

Synthesis of Sn₂L₂. To a flask containing 4,4'-(1,4-phenylene)bis-1,3-dithiol-2-one **2** (500 mg, 1.61 mmol) was added under inert atmosphere a solution of NaOMe (freshly prepared from sodium (220 mg, 9.67 mmol) in 25 mL of dry methanol). The reaction mixture was stirred for 1h30 at 40°C then cooled at room temperature and Bu₂SnCl₂ (3.22 mmol, 980 mg) was added. The reaction mixture was stirred overnight. The precipitate was filtered off and washed with water, ethanol and diethylether to afford compound **Sn₂L₂** (500mg, 0.69 mmol) as a pale yellow powder. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution. Yield: 43%; Mp = 140°C; ¹H NMR (300 MHz) δ 0.94 (t, 12H, ³J = 7.3 Hz, CH₃), 1.40 (m, 8H, CH₃-CH₂), 1.53-1.67 (m, 8H, CH₃-CH₂-CH₂), 1.68-1.79 (m, 8H, Sn-CH₂), 6.79 (s, 2H, =CH), 7.47 (s, 4H, Ar); ¹³C NMR (75 MHz) δ 13.6 (CH₃), 22.4 (CH₃-CH₂), 26.6 (CH₃-CH₂-CH₂), 27.8 (Sn-CH₂), 117.4 (SCH=C), 126.7 (4Ar), 136.5 (2Ar), 139.2 (SC=CH); UV-vis (CH₂Cl₂) λ_{max}(nm) (ε[M⁻¹.cm⁻¹])= 247(25590), 346(19920); HRMS (ESI) calcd for C₂₆H₄₂S₄NaSn₂ [M+Na]⁺: 745.01056. Found: 745.0107; Anal calcd for C₂₆H₄₂S₄Sn₂: C, 43.36; H, 5.88; S, 17.80. Found: C, 43.52; H, 5.69; S, 17.92.

Synthesis of SnL₁Mo and Mo₂L₁. To a Schlenk tube, the bis(2,2-dimethyl[3,4-d]-1,3,2-dithiastannolo)biphenyl **Sn₂L₁** (200 mg, 0.27 mmol) with Cp₂MoCl₂ (320 mg, 1.08 mmol) were placed under vacuum for 1h. Then the solids were solubilized in a dry and degassed mixture of THF and CHCl₃ (10 mL of each solvent). The solution was stirred overnight at 50°C. The solvent was evaporated and the resulting solid was purified by flash chromatography on silica gel using chloroform/ethyl acetate (1/1) as eluent. Complexes **SnL₁Mo** (30 mg, 0.04 mmol) and **Mo₂L₁** (70 mg, 0.095 mmol) were obtained as dark red powder respectively in 15 and 35 % yield.

SnL1Mo: (Rf=0.2); Mp = 154°C; ^1H NMR (300 MHz) δ 7.70 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.41 (dd, J = 23.6, 8.1 Hz, 2H), 7.11 (m, 1H), 6.95 (m, 1H), 5.32 (s, 10H), 1.80 – 1.63 (m, 8H), 1.42 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H); NMR ^{13}C (75 MHz) δ 13.6 (CH_3), 21.9 ($\text{CH}_3\text{-}\underline{\text{CH}_2}$), 26.7 ($\text{CH}_3\text{-CH}_2\text{-}\underline{\text{CH}_2}$), 27.9 (Sn- CH_2), 98.3 (Cp), 120.7, 122.7, 126, 127.8, 128.1, 130 (6CH Ar), 134, 136.1, 137.4, 138.6, 144.6, 145.8; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\text{nm})$ ($\epsilon[\text{M}^{-1}.\text{cm}^{-1}]$) = 260(18161), 462(3004); HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{S}_4\text{SnMo}$ $[\text{M}]^+$: 739.96139. Found: 739.9617; Anal calcd for $\text{C}_{30}\text{H}_{34}\text{S}_4\text{SnMo}$: C, 48.86; H, 4.65; S, 17.39. Found: C, 48.73; H, 4.70; S, 17.25.

Mo2L1: (Rf=0.5); Mp>250°C; ^1H NMR (300 MHz) δ 7.58 (d, J = 1.9 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.99 (m, 2H), 5.31 (s, 10H). ^{13}C NMR spectrum could not be obtained due to limited solubility of the compound. UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\text{nm})$ ($\epsilon[\text{M}^{-1}.\text{cm}^{-1}]$) = 358(17400), 476(3757). HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{26}\text{S}_4\text{Mo}_2$ $[\text{M}]^+$: 733.90255. Found: 733.9023; Anal calcd for $[\text{C}_{32}\text{H}_{26}\text{S}_4\text{Mo}_2 + 1/2\text{CH}_2\text{Cl}_2]$: C, 50.49; H, 3.52; S, 16.59. Found: C, 50.81; H, 3.86; S, 16.32.

Synthesis of Mo2L2. To a flask containing bis-dithiolone **1** (180 mg, 0.58 mmol) was added under inert atmosphere a solution of NaOMe (freshly prepared from sodium (80 mg, 3.48 mmol) in 15 mL of dry methanol). The reaction mixture was stirred for 1h30 at 40°C then cooled at room temperature and Cp_2MoCl_2 (1.16 mmol, 344 mg) was added. The reaction mixture was heated at 60°C overnight. The precipitate was filtered off and washed with water, ethanol and diethylether to afford compound **Mo2L2** (350 mg, 0.49 mmol) as a black powder. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of a saturated chloroform solution. Yield: 85%; Mp>250°C; ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 300 MHz) δ 5.35 (s, 20H, Cp), 6.67 (s, 2H, =CH), 7.41 (s, 4H, Ar); ^{13}C NMR spectrum could not be obtained due to limited solubility of the compound; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\text{nm})$ ($\epsilon[\text{M}^{-1}.\text{cm}^{-1}]$): 259 (22100), 387(4000), 572(10940); HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{26}\text{S}_4\text{Mo}_2$ $[\text{M}]^+$: 709.90255. Found:

709.9024; Anal calcd for $[C_{30}H_{26}S_4Mo_2 + \frac{1}{2} CHCl_3]$: C, 48.05; H, 3.57; S, 17.27. Found: C, 47.80; H, 3.49; S, 16.73.

Crystallography

Data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator) for **2**, **Sn₂L2**, **Mo₂L1** and **Mo₂L2**. The structures were solved by dual-space algorithm using the *SHELXT* program,²⁷ and then refined with full-matrix least-square methods based on F^2 (*SHELXL*).²⁸ For **Mo₂L1**, the contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,²⁹ implemented as the *SQUEEZE* option in *PLATON*.³⁰ A new data set, free of solvent contribution, was then used in the final refinement. For the four structures, all non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Crystallographic data on X-ray data collection and structure refinements are given in Table 3.

Table 3 Crystallographic data for **2**, **Sn₂L2**, **Mo₂L1** and **Mo₂L2**

Compound	2	Sn₂L2	Mo₂L1.0.5CH₂Cl₂	Mo₂L2.0.5CHCl₃
Formula	C ₁₂ H ₆ O ₂ S ₄	C ₂₆ H ₄₂ S ₄ Sn ₂	C ₃₃ H ₂₈ Cl ₂ Mo ₂ S ₄	C ₃₁ H ₂₇ Cl ₃ Mo ₂ S ₄
FW (g.mol ⁻¹)	310.41	720.21	815.57	825.99
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	3.9718(9)	10.9394(14)	13.5443(17)	17.3775(17)
<i>b</i> (Å)	7.1545(14)	13.0029(17)	18.625(2)	14.8924(13)
<i>c</i> (Å)	10.6205(17)	13.3422(16)	14.1052(17)	11.7236(12)
α (°)	80.822(7)	65.420(4)	90	90
β (°)	79.994(8)	76.584(4)	115.704(4)	96.300(4)
γ (°)	88.795(9)	72.110(4)	90	90
<i>V</i> (Å ³)	293.39(10)	1630.5(4)	3206.0(7)	3015.7(5)
<i>T</i> (K)	150(2)	2	150(2)	150(2)
<i>Z</i>	1	250(2)	4	4
<i>D</i> _{calc} (g·cm ⁻³)	1.757	1.467	1.690	1.819
μ (mm ⁻¹)	0.796	1.800	1.233	1.397
Total reffs.	5774	36783	31356	22944
Uniq. reffs. (<i>R</i> _{int})	1330(0.0781)	7386(0.0504)	7236 (0.0799)	6859 (0.0666)
Unique reffs.(<i>I</i> >2σ(<i>I</i>))	1139	5639	5458	4676
<i>R</i> ₁ , <i>wR</i> ₂	0.0909, 0.2900	0.0580, 0.1454	0.0438, 0.0981	0.0846, 0.1872
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1010, 0.3015	0.0807, 0.1684	0.0690, 0.1090	0.1320, 0.2152
GoF	1.076	1.025	1.049	1.093

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Supporting Information Available

X-ray crystallographic files in CIF format, NMR, HRMS spectra and computational details.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Competing financial Interest

The authors declare no competing financial interest.

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