Synthesis and Electrochemical and Spectroscopic Properties of Molybdenum Complexes Bearing 5-Alkoxythiophene or -bithiophene Groups

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trans-[MoF{NN=CH(5'-R-thienyl)}(dppe)₂][BF₄] (R = OMe and OEt) and trans-[MoF{NN=CH(5'-R-2,2'-bithienyl)}-(dppe)₂][BF₄] (R = OMe, OEt and OiPr) were synthesised in good yields by treating 5-alkoxy-2-formylthiophenes and 5'-alkoxy-5-formyl-2,2'-bithiophenes, respectively, with the hydrazido(2–) complex trans-[MoF(NNH₂)(dppe)₂][BF₄]. The electrochemical, spectroscopic and solvatochromic properties

of these compounds were studied. These results suggest that efficient π -conjugated systems are obtained due to the lowenergy charge-transfer between the metal atom and the heterocyclic moieties.

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Introduction

There is considerable interest in the synthesis of new organic and organometallic materials with large second-order optical nonlinearities because of their potential applications in telecommunications, optical computing, optical storage and optical information processing.^[1–3]

Structural, redox and photophysical properties can easily be tuned in organometallic compounds. Consequently, they have been explored in the design of materials for nonlinear optical (NLO) applications.^[4,5] In this case, for a molecule to be of interest it must present an excited state of similar energy to the ground state, as well as a dipolar moment that is quite different in the ground and excited states.^[6,7] These requirements are satisfied in asymmetric conjugated complexes containing electron-acceptor and electron-donor groups connected by a conjugated π system.^[8,9] For example, metal complexes based on nitrosylmolybdenum and -tungsten moieties stabilised by tris(3,5-dimethylpyrazolyl)borate and attached to phenolato or anilido groups are strongly polarised and may therefore be able to act as electron termini of dipolar complexes having second-order NLO properties.^[7] Thiophene and bithiophene chromophores exhibit greater β second-order polarisabilities compared to those of biphenyls or stilbenes.^[10] Transition metal

complexes of the general type *trans*- $[MX(NNR)(dppe)_2]^+$ [M = Mo or W; X = halide; dppe = 1,2-bis(diphenylphosphanyl)ethane; R = heterocyclic group] are particularly attractive because the conjugated structure, including the central metal atom and the square-planar {M(dppe)_2} assembly, is robust.^[11,12]

In this paper we wish to report the synthesis and the electrochemical, spectroscopic and solvatochromic properties of the new electron-donor– π -acceptor systems *trans*-[MoF{NN=CH(thienyl-5'-alkoxy)}(dppe)₂][BF₄] **6** and **8** (alkoxy = OMe and OEt, respectively) and *trans*-[MoF{NN=CH(bithienyl-5'-alkoxy)}(dppe)₂][BF₄] **7**, **9** and **10** (alkoxy = OMe, OEt and O*i*Pr, respectively). As far as we know, the synthesis and the characterisation of molybdenum complexes bearing 2-alkoxythienyl groups and 2-alkoxybithienyl groups has not been reported previously.

Results and Discussion

Synthesis

As part of our ongoing effort to develop chromophores for nonlinear optical applications,^[13–16] we synthesised several donor–acceptor 5,5'-disubstituted 2,2'-bithiophenes^[13] by functionalisation of the corresponding 5-alkoxybithiophenes.^[17] We have recently reported the synthesis of the 5'-alkoxy-5-formyl-2,2'-bithiophene derivatives **2**, **4** and **5** (alkoxy = OMe, OEt and O*i*Pr, respectively), which made these compounds available in reasonable amounts.^[13] Indeed, we were able to use these compounds successfully as substrates for the synthesis of the molybdenum complexes. The versatile method to form carbon–nitrogen bonds involves the initial conversion of *trans*-[Mo(N₂)₂-

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(dppe)₂] into the hydrazido(2–) complex trans- $[MoF(NNH_2)(dppe)_2][BF_4]$, which then undergoes an electrophilic attack at the terminal nitrogen atom. It can therefore be used as a key intermediate in the preparation of organonitrogen complexes by subsequent reactions with organic carbonyl compounds.^[18] Condensation with 5-alkoxy-2-formylthiophene [alkoxy = OMe (1) or OEt (3)] or 5'alkoxy-5-formyl-2,2'-bithiophene [alkoxy = OMe (2), OEt(4) or OiPr (5)] gave the molybdenum complexes 6–10 bearing the alkoxythiophenic or alkoxybithiophenic group, respectively, in good yields (65-78%; Scheme 1).



Scheme 1.

The structures of these complexes were confirmed by the usual spectroscopic methods. Each diazenido [hydrazido-(-2)] complex shows a characteristic band in the 1515–1550 cm⁻¹ region of its FTIR spectrum that can be assigned to v(C=N).^[19] Their *trans* stereochemistry was confirmed by the ³¹P{¹H}NMR spectra, which show a single resonance.

Electrochemistry

Electrochemical data for compounds 1–5 are summarised in Table 1. Cyclic voltammetry shows an irreversible singleelectron oxidation process (E_{pa}) which can be attributed to the formation of the radical cation of the heterocyclic part. As the HOMO levels in the heterocyclic part increase with the donor effect of the alkoxy groups along the series OMe < OEt < OiPr, the ease of oxidation increases gradually. The oxidation processes of the bithienyl groups are systematically shifted to less positive potentials than those of the thienyl groups. This fact can be explained by the stabilisation of the cation radical due to its higher delocalisation on the bithienvl moiety. At low potentials (< -2 V vs. fc/fc⁺) these compounds exhibit one irreversible single-electron process $(-E_{pr})$, which generates a radical anion. The electron goes into a π^* -antibonding orbital of the heterocycle. This electron injection occurs at more negative potentials as the alkoxy group is an electron donor and its delocalisation on the heterocyclic part is difficult.

Electrochemical data for complexes 6-10 are collected in Table 2. A typical cyclic voltammogram of trans- $[MoF{NN=CH(5'-OEt-2,2'-bithienyl)}(dppe)_2][BF_4]$ (9) in DMF/0.1 M [Bu₄N][BF₄] at a vitreous carbon electrode is shown in Figure 1. The molybdenum complexes show three single-electron oxidation processes. The first $(E_{a1/2})$ and second processes (E_{pal}) are reversible and irreversible, respectively, and correspond to the Mo^{IV}/Mo^V and Mo^V/Mo^{VI} waves. Controlled potential coulometry of the first oxidation step confirms a single-electron process. The resulting solution displays a cyclic voltammetric profile that resembles the original one. The parent complex trans-[MoF(NNH₂)(dppe)₂][BF₄] has only one irreversible wave at 0.34 V vs. fc⁺/fc. A comparison of the values obtained for 6-10 with that of the parent complex shows that the donor effect of the alkoxy substituent stabilises Mo^V completely and Mo^{VI} partially. However, the oxidation potentials of compounds 7 and 9, which have a bithiophenic link, are slightly higher (40 mV) than those of 6 and 8, which bear a thiophenic link. This fact can be explained by metalto-heterocycle π^* -orbital back-donation via the hydrazido ligand. This back-donation increases in the case of a bithiophenic link, which contributes to the stabilisation of the metal-centred HOMO orbital. In both cases this suggests a

Table 1. Electrochemical and electronic spectroscopic data for the thiophenic and bithiophenic groups 1-5.

			Electrochemical data ^[a]		Electronic spectroscopic data ^[b]	
Compound	R	п	Reductions $-E_{\rm pr}$ [V]	Oxidations E_{pa} [V]	λ_{\max} [nm]	$10^{-3} \varepsilon [\mathrm{M}^{-1} \mathrm{cm}^{-1}]$
1	OMe	1	2.30	0.86	310	24.7
2	OMe	2	2.00	0.76	362	16.3
3	OEt	1	2.34	0.82	316	21.2
4	OEt	2	2.08	0.74	391	24.5
5	O <i>i</i> Pr	2	2.14	0.73	393	23.8

[a] All measurements were recorded at 298 K in degassed acetonitrile solutions with $[Bu_4N][BF_4]$ (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 Vs⁻¹. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted into V vs. the ferrocene/ferrocenium couple $[E_{1/2}(fc^+/fc) = 0.38 \text{ V/SCE}]$. [b] Measured in acetonitrile.

C 1	D	D	Electrochemical data ^[a]			Electronic spectroscopic data ^[b]		
Complex R		n	Reduction		Oxidations			
			$-E_{c1/2}$ [V]	$E_{a1/2}$ [V]	$E_{\text{pa1}}[V]$	$E_{\rm pa2}$ [V]	λ _{max} [nm]	$10^{-3} \varepsilon [M^{-1} cm^{-1}]$
6	OMe	1	1.45	0.24	0.47	0.87	469	17.2
7	OMe	2	1.36	0.28	0.53	0.76	482	17.4
8	OEt	1	1.50	0.20	0.42	0.83	474	18.1
9	OEt	2	1.40	0.24	0.50	0.74	497	16.7
10	O <i>i</i> Pr	2	1.43	0.20	0.47	0.74	496	19.3

Table 2. Electrochemical and electronic spectroscopic data for complexes 6-10.

[a] All measurements were recorded at 298 K in degassed acetonitrile solutions with $[Bu_4N][BF_4]$ (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 Vs⁻¹. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted into V vs. the ferrocenium/ferrocene couple $[E_{1/2}(fc^+/fc) = 0.38 \text{ V/SCE}]$. [b] Measured in acetonitrile.

 π -conjugated system between the metal acceptor group and the alkoxythiophene and -bithiophene moieties. In complexes **6–10** the oxidation potentials (E_{pa2}) of the heterocyclic parts are not significantly modified in comparison with those of the corresponding compounds **1–5**. The reduction of the complexes occurs in a quasi-reversible one-electron process ($-E_{c1/2}$, $\Delta E_p = 200$ mV). For **7**, **9** and **10**, with a bithiophenic linker, the reduction potentials are shifted to higher values than for **6** and **8**. The corresponding stabilisation of the LUMO (π^*) ligand orbital does not correspond to an electron-donor effect of this link, but to a better delocalisation of the injected electron into the ligand on the bithiophene moiety via the imino bridge.



Figure 1. Cyclic voltammogram of *trans*-[MoF{NN=CH(5'-OEt-2,2'-bithienyl)}(dppe)_2][BF₄] (9) in DMF/0.1 \times [Bu₄N][BF₄] at a vitreous carbon electrode (area = 0.049 cm²). Scan rate: 100 mV s⁻¹; concentration of complex: 2.3 mM.

UV/Vis and Solvatochromic Studies

The UV/Vis spectroscopic data for heterocycles 1–5 are presented in Table 1. The electronic absorption spectra show an absorption band in the near-UV region due to the π - π * transitions in the heterocyclic parts. The bithienyl groups show red-shifted absorption maxima relative to the thienyl groups. This is due to better delocalisation of the excited electron in the π *-orbital, which causes its stabilisation. Moreover, the position of these bands is influenced by the donor effect of the alkoxy group, which lowers the energy gap.

The UV/Vis spectroscopic data for complexes 6-10 are summarised in Table 2. The parent complex trans-[MoF(NNH2)(dppe)2][BF4] shows a broad band at around 275 nm corresponding to a transition in the dppe ligand. Complexes 6-10, which bear heterocyclic groups, show an absorption band in the visible region because the molybdenum part lowers the energies of the transition in the heterocycle. For example, the absorption maximum of 1, which appears at 310 nm, is red-shifted to 469 nm for complex 6. The intramolecular charge-transfer process, which originates in the Mo part and is propagated through the π -conjugated spacer ligand [hydrazido(2-)], gives rise to a considerable bathochromic shift of the alkoxythiophenic and -bithiophenic transitions (Figure 2). For these complexes, the alkoxy group effect and the better delocalisation in the bithienyl groups induce modifications of their electronic spectra similar to those described for compounds 1-5. The influence of the incorporation of thiophene moieties in push-pull compounds on the charge-transfer properties has been described previously.[20]



Figure 2. UV/Vis spectra of 2-formyl-5-methoxythiophene (1) and *trans*-[MoF{NN=CH(5'-methoxythienyl)}(dppe)₂][BF₄] (6) in ace-tonitrile, demonstrating the effect of the Mo part on the absorption maxima between 300 and 700 nm.

Table 3. Solvatochromic data (λ_{max} [nm] and \tilde{v}	¹ [cm ⁻¹] of the charge-transfer	r band) for complexes 6–10 ir	n selected solvents in comparison
with the π^* values of Kamlet and Taft. ^[24]			

Complex	THF (0.58) $\lambda_{\max}, \tilde{v}_0$	Acetone (0.71) $\lambda_{\max}, \tilde{v}_0$	Solvent (π^*) Acetonitrile (0.75) $\lambda_{\max}, \tilde{v}_0$	$\begin{array}{c} CH_2Cl_2 \ (0.82) \\ \lambda_{max}, \ \tilde{v}_0 \end{array}$	DMSO (0.88) $\lambda_{\rm max}, \tilde{v}_0$
6	466, 21459	468, 21413	469, 21322	471, 21231	474, 21097
7	479, 20877	481, 20790	482, 20747	485, 20619	488, 20492
8	479, 20877	482, 20747	484, 20661	487, 20534	490, 20408
9	493, 20284	495, 20202	497, 20121	501, 19960	505, 19802
10	491, 20366	494, 20243	496, 20161	499, 20040	502, 19920

In general, the stronger the donor and/or acceptor group, the smaller the energy difference between the ground and excited states and the longer the wavelength of the absorption. According to Zyss,^[21] the increase in the β -values characteristic of the NLO effects is accompanied by an increase of λ_{max} in the UV/Vis spectra.

Solvatochromism is easily quantified by UV/Vis spectroscopy and is particularly suitable for the empirical determination of the polarity of a solvent^[22,23] on a molecularmicroscopic level. To evaluate the intermolecular forces between the solvents and the solute molecules we recorded absorption spectra of all complexes in five polar solvents of different solvation character (Table 3). Due to the insolubility of complexes **6–10** in apolar solvents the solvatochromic study of these compounds was only performed in polar solvents such as tetrahydrofuran, acetone, acetonitrile, dichloromethane and dimethyl sulfoxide. The electronic excitations are governed by a positive solvatochromism with increasing solvent polarity, indicating dipole changes within the ground excited state.

Good correlation with the π^* parameters defined by Kamlet and Taft^[24] was obtained. Table 4 summarises the results of the linear regression analyses of absorption maxima for complexes **6–10**. The most important values of the linear relationship between absorption maxima and π^* are the correlation coefficient, *r*, and the slope, *s*, which describes the extent of solvatochromism from $\pi^* = 0.58$ (tetrahydrofuran) to $\pi^* = 1.00$ (DMSO). As shown in Table 4, the greatest value for *s* is found for complex **9**. The change in dipole moment on electronic excitation is shown to be

Table 4. Correlation of the UV/Vis absorption maxima of complexes 6--10 and the solvent parameter $\pi^{*,[a]}$

Complexes	Regression analysis ^[b]				
-	$\tilde{v}_0 [\mathrm{cm}^{-1}]$	S	r		
6	22013	-917.62	0.9760		
7	21448	-962.61	0.9843		
8	21590	-1158.20	0.9814		
9	20989	-1196.40	0.9863		
10	20997	-1101.80	0.9760		

[a] Applied solvents (π^* value): THF (0.58), acetone (0.71), acetonitrile (0.75), dichloromethane (0.82) and dimethyl sulfoxide (1.0). [b] Intercept, slope, and correlation *r* of the linear solvation energy relationship, according to the equation $v_{\text{max}} = v_0 + s\pi^*$. oriented parallel to the transition dipole and is, moreover, constant over the whole charge-transfer band.

Conclusions

We have described the synthesis and characterisation of molybdenum complexes connected via a hydrazido(2–) bridge to alkoxythiophenic or alkoxybithiophenic groups. Their electrochemical, spectroscopic and solvatochromic behaviours exhibit an intramolecular charge-transfer effect. These new complexes are promising candidates for developing novel NLO materials.

Experimental Section

General: All reactions were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying agents under dinitrogen. The syntheses of 5'-alkoxy-5-formyl-2,2'-bithiophenes^[13] and complexes trans- $[Mo(N_2)(dppe)_2]$ and *trans*- $[MoF(NNH_2)(dppe)_2]^{[17]}$ have already been described. The NMR spectra were obtained with a Varian Unity Plus Spectrometer at 300 MHz using the solvent peak as internal reference. Infrared spectra were recorded with a Perkin-Elmer 1600 FTIR spectrophotometer. UV/Vis absorption spectra were obtained with a Shimadzu UV/2501PC spectrophotometer. High-resolution mass spectra (HRMS) were obtained with a GV AutoSpec spectrometer with *m*-nitrobenzyl alcohol (NBA) as matrix. Elemental analyses were performed with a Leco CHNS-932 analyser. Voltammetric measurements were performed with a potentiostat/galvanostat (AUTOLAB /PSTAT 12 with low current module ECD from ECO-CHEMIE) and the data processed with the General Purpose Electrochemical System software package (ECO-CHEMIE). Three-electrode two-compartment cells equipped with vitreous carbon-disc working electrodes, a platinumwire secondary electrode and a silver-wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The ferrocenium-ferrocene redox couple was used as a secondary internal reference. The concentrations of the compounds were typically 1-2 mM, and 0.2 M [Bu₄N][BF₄] was used as the supporting electrolyte in N,N-dimethylformamide solvent. The potential was measured with respect to ferrocinium/ferrocene as an internal standard. Controlled-potential electrolyses were carried out in an Htype cell with a vitreous carbon working electrode as described previously.^[12]

General Procedure for the Preparation of Complexes 6–10: The complex *trans*-[MoF(NNH₂)(dppe)₂][BF₄] (0.2 g, 0.19 mmol) was dis-

solved in THF (20 mL) at room temperature. Formyl ligands 1–5 (0.40 mmol) were added in excess to the solution, which was stirred for 28 h. The volume of the solution was then reduced to about 5 mL and the precipitates were filtered off. These solids were dissolved in CH₂Cl₂ and filtered through a pad of Celite. The solutions were concentrated to dryness and the solids obtained washed with cold THF (3×5 mL), then Et₂O (2×3 mL), and dried in vacuo to give complexes 6–10 as coloured solids. In all cases, the solids thus obtained were crystallised from CH₂Cl₂/Et₂O.

6: Pink solid. Yield: 0.16 g (73%). ¹H NMR (300 MHz, CDCl₃): δ = 2.4–2.8 (m, 8 H, 2×PCH₂CH₂P), 3.4 (s, 3 H, OCH₃), 4.6 (s, 1 H, N=CH), 6.8–7.4 (m, 42 H, 40 H and 2 H of thienyl) ppm. ³¹P{¹H}NMR (121.7 MHz, CDCl₃): δ = –100.3 (s, MoP) ppm. IR (KBr): \tilde{v} = 1550 (N=C) cm⁻¹. HRMS (NBA): calcd. for C₅₈H₅₄FMoN₂OP₄S [M]⁺ 1067.1945; found 1067.1968. C₅₈H₅₄BF₅MoN₂OP₄S (1152.8): calcd. C 60.43, H 4.72, N 2.43, S 2.78; found C 60.78, H 4.83, N 2.51, S 2.83.

7: Orange solid. Yield: 0.18 g (77%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.4-2.7$ (m, 8 H, 2×PCH₂CH₂P), 3.6 (s, 3 H, OCH₃), 4.5 (s, 1 H, N=CH), 6.8-7.4 (m, 44 H, 40 H of phenyl and 4 H of bithienyl) ppm. ³¹P{¹H}NMR (121.7 MHz, CDCl₃): $\delta = -100.1$ (s, MoP) ppm. IR (KBr): $\tilde{v} = 1534$ cm⁻¹ (N=C). HRMS (NBA): calcd. for C₆₂H₅₆FMoN₂OP₄S₂ [M]⁺ 1149.1823; found 1149.1816. C₆₂H₅₆BF₅MoN₂OP₄S₂ (1234.9): calcd. C 60.30, H 4.57, N 2.27, S 5.19; found C 60.47, H 4.72, N 2.41, S 5.25.

8: Pink solid. Yield: 0.15 g (67%). ¹H NMR (300 MHz, CDCl₃): δ = 1.6 (t, J = 6.4 Hz, 3 H, OCH₂CH₃), 2.4–2.7 (m, 8 H, 2×PCH₂CH₂P), 3.5 (q, J = 6.4 Hz, 2 H, OCH₂CH₃), 4.5 (s, 1 H, N=CH), 6.9–7.5 (m, 42 H, 40 H of phenyl and 2 H of thienyl) ppm. ³¹P{¹H}NMR (121.7 MHz, CDCl₃): δ = –100.2 (s, MoP) ppm. IR (KBr): \tilde{v} = 1546 cm⁻¹ (N=C). HRMS (NBA): calcd. for C₅₉H₅₆FMoN₂OP₄S [M]⁺ 1081.2102; found 1081.2118. C₅₉H₅₆BF₅MoN₂OP₄S (1166.81): calcd. C 60.73, H 4.84, N 2.40, S 2.75; found C 60.48, H 4.87, N 2.59, S 5.71.

9: Orange solid. Yield: 0.18 g (78%). ¹H NMR (300 MHz, CDCl₃): $\delta = 1.8$ (t, J = 6.3 Hz, 3 H, OCH₂CH₃), 2.4–2.7 (m, 8 H, $2 \times PCH_2CH_2P$), 3.8 (q, J = 6.3 Hz, 2 H, OCH₂CH₃), 4.3 (s, 1 H, N=CH), 7.0–7.6 (m, 44 H, 40 H of phenyl and 4 H of bithienyl) ppm. ³¹P{¹H}NMR (121.7 MHz, CDCl₃): $\delta = -99.7$ (s, MoP) ppm. IR (KBr): $\tilde{v} = 1515$ cm⁻¹ (N=C). HRMS (NBA): calcd. for C₆₃H₅₈FMoN₂OP₄S₂ [M]⁺ 1163.1979; found 1163.1929. C₆₃H₅₈BF₅MoN₂OP₄S₂ (1248.9): calcd. C 60.59, H 4.68, N 2.24, S 5,14; found C 60.82, H 4.77, N 2.44, S 5.19.

10: Orange solid. Yield: 0.16 g (65%). ¹H NMR (300 MHz, CDCl₃): $\delta = 1.5$ [d, J = 6.1 Hz, 6 H, OCH(CH₃)₂], 2.3–2.7 (m, 8 H, 2×PCH₂CH₂P), 3.4 [m, 1 H, OCH(CH₃)₂], 4.2 (s, 1 H, N=CH), and 6.9–7.6 (m, 44 H, 40 H of phenyl and 4 H of bithienyl) ppm. ³¹P{¹H}NMR (121.7 MHz, CDCl₃): $\delta = -99.8$ (s, MoP) ppm. IR (KBr): $\tilde{v} = 1519$ cm⁻¹ (N=C). HRMS (NBA): calcd. for C₆₄H₆₀FMoN₂OP₄S₂ [M]⁺ 1177.2136; found 1177.2101. C₆₄H₆₀BF₅MoN₂OP₄S₂ (1263.0): calcd. C 60.87, H 4.79, N 2.22, S 5.08; found C 61.12, H 4.88, N 2.15, S 5.17.

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