

# Synthesis, electrochemical and spectroscopic properties of molybdenum complexes bearing 5-alkoxy-thiophenic or- bithiophenic groups

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*Trans*-[FMo{NN=CH(5'-R-thienyl)}(dppe)<sub>2</sub>][BF<sub>4</sub>] (R = OMe and OEt) and *trans*-[FMo{NN=CH(5'-R-2,2'-bithienyl)}(dppe)<sub>2</sub>][BF<sub>4</sub>] (R = OMe, OEt and O(*i*Pr)) were synthesised in good yields by reacting 2-formyl-5-alkoxythiophenes and 5-formyl-5'-alkoxy-2,2'-bithiophenes respectively, with hydrazido(2-) complex, *trans*-[MoF(NNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>]. The electrochemical, spectroscopic and solvatochromic properties of these compounds were studied. These results suggest that efficient  $\pi$  conjugated systems were obtained due to the low energy charge transfer between the metal 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 potential applications in telecommunications, optical computing, optical storage and optical information processing.<sup>[1-3]</sup>

In organometallic compounds, structural, redox and photophysical properties can be easily tuned. Consequently, they have been explored in the design of materials for non linear optic (NLO) applications.<sup>[4-5]</sup> 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 quite different in the ground and excited states.<sup>[6-7]</sup> These requirements are satisfied in asymmetric conjugated complexes containing electron acceptor and electron donor groups connected by a conjugated  $\pi$  system.<sup>[8-9]</sup> For example, metal complexes based on molybdenum and tungsten nitrosyl moieties, stabilised by tris(3,5-

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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.<sup>[7]</sup> Thiophene and bithiophene chromophores exhibit enhanced  $\beta$  second-order polarisabilities compared to those of biphenyls or stilbenes.<sup>[10]</sup> Transition metal complexes of the general type *trans*-[MX(NNR)(dppe)<sub>2</sub>]<sup>+</sup> [M = Mo or W; X = halide; dppe = 1,2-bis(di-arylphosphino)ethane, R like a heterocyclic group, are particularly attractive because the conjugated structure, including the central metal atom and the square-planar {M(dppe)<sub>2</sub>} assembly, is robust.<sup>[11-12]</sup>

In this paper we wish to report the synthesis, the electrochemical, spectroscopic and solvatochromic properties of the new electron donor- $\pi$ -acceptor systems: *trans*-[FMo{NN=CH-(thienyl-5'-alkoxy)}(dppe)<sub>2</sub>][BF<sub>4</sub>] **6** and **8** (alkoxy = OMe and OEt respectively) and *trans*-[FMo{NN=CH-(bithienyl-5'-alkoxy)}(dppe)<sub>2</sub>][BF<sub>4</sub>] **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 have not been previously reported.

## Results and Discussion

### Synthesis

As part of our ongoing effort to develop chromophores for non-linear optical applications<sup>[13-16]</sup> we synthesised several donor-acceptor 5,5'-disubstituted 2,2'-bithiophenes<sup>[13]</sup> by functionalisation of the corresponding 5-alkoxy-bithiophenes.<sup>[17]</sup> We have recently reported the synthesis of 5-formyl-5'-alkoxy-2,2'-bithiophene derivatives **2**, **4** and **5** [alkoxy=OMe, OEt and O(*i*Pr) respectively] which made these compounds available in reasonable amounts.<sup>[13]</sup> Indeed, we were able to use these compounds successfully as substrates for the synthesis of the molybdenum complexes. The versatile method to make carbon-nitrogen bonds involves the initial conversion of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] into the hydrazido(2-) complex *trans*-[FMo(NNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>]. This complex can undergo an electrophilic attack at the terminal nitrogen atom. It can therefore be used as key intermediate in the preparation of organo-nitrogen complexes by subsequent reactions with organic carbonyl compounds.<sup>[18]</sup> Condensation with 2-formyl-5-alkoxythiophene (alkoxy = OMe **1** or OEt **3**) or 5-formyl-5'-alkoxy-2,2'-bithiophene (alkoxy = OMe **2**, OEt **4** or O(*i*Pr) **5**) gave the molybdenum complexes **6-10** bearing the alkoxythiophenic or alkoxybithiophenic group respectively (Scheme 1), in good yields (65-78%).

The structures of these complexes were confirmed by the usual spectral criteria. Each diazenido (hydrazido(-2)) complex shows a characteristic band in the 1515-1550 cm<sup>-1</sup> region of its FTIR spectrum, which is assigned to  $\nu(\text{C}=\text{N})$ .<sup>[19]</sup> Their *trans* stereochemistry was confirmed by their <sup>31</sup>P-<sup>1</sup>H}NMR spectra which show a single resonance.

## (SCHEME 1)

### Electrochemistry

Electrochemical data for compounds **1-5** are summarised in Table 1. Cyclic voltammetry shows an irreversible monoelectronic 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  $OMe < OEt < O(iPr)$ , 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 bithienyl moiety. At low potentials ( $< -2$  V vs.  $fc/fc^+$ ) these compounds exhibit one irreversible monoelectronic process ( $-E_{pr}$ ) which generates a radical anion. The electron goes into a  $\pi^*$  antibonding orbital of the heterocycle. This electron injection occurs at more negative potentials as the alkoxy group is 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*-[FMo{NN=CH(5'-OEt-2,2'-bithienyl)}(dppe)<sub>2</sub>][BF<sub>4</sub>] in DMF-0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>], complex **9**, at a vitreous carbon electrode is shown in Figure 1. The molybdenum complexes show three monoelectronic oxidation processes. The first ( $E_{a1/2}$ ) and the second processes ( $E_{pa1}$ ) are reversible and irreversible respectively and correspond to the Mo<sup>IV</sup>/Mo<sup>V</sup> and Mo<sup>V</sup>/Mo<sup>VI</sup> wave successively. Controlled potential coulometry of the first oxidation step confirms a monoelectronic process. The resulting solution displays a cyclic voltammetric profile that resembles the original one. The parent complex *trans*-[FMo(NNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>] has only one irreversible wave at 0.34 V vs.  $fc^+/fc$ . Comparison of values obtained for **6-10** with that of the parent complex shows that the donor effect of the alkoxy substituent stabilises Mo<sup>V</sup> thoroughly and Mo<sup>VI</sup> partially. However, oxidation potentials of compounds **7, 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 metal to heterocyclic group  $\pi^*$  orbital backdonation via the hydrazido ligand. This backdonation 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  $\pi$ -conjugated system between the metallic acceptor group and the alkoxy -thiophene 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 ( $\pi^*$ ) 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.

(TABLE 1)

(TABLE 2)

### UV-Visible and solvatochromic studies

The UV-visible spectral data for heterocycles **1-5** are presented in Table 1. Electronic absorption spectra show an absorption band in the near UV-region due to the  $\pi$ - $\pi^*$  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  $\pi^*$  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-visible spectral data for complexes **6-10** are summarised in Table 2. The parent complex *trans*-[MoF(NNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>] shows a broad band at *ca* 275 nm corresponding to a transition in the dppe ligand. Complexes **6-10** bearing heterocycle 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 Mo part and is propagated through the  $\pi$ -conjugated spacer ligand (hydrazido(-2)), gives rise to a considerable bathochromic shift of the alkoxy -thiophenic and -bithiophenic transitions (Figure 2). For these complexes the alkoxy group effect and the better delocalisation in 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 previously described.<sup>[20]</sup>

In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. According to Zyss<sup>[21]</sup> the increase in the  $\beta$  values characteristic of the NLO effects is accompanied by an increase of the  $\lambda_{\text{max}}$  in the UV-visible spectra.

Solvatochromism is easily quantified by UV-visible spectroscopy and is particularly suitable for the empirical determination of the polarity of a solvent<sup>[22, 23]</sup> on a molecular-microscopic level. To evaluate the intermolecular forces between the solvents and the soluted 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 dimethylsulfoxide. The electronic excitations are governed by a positive solvatochromism with increasing solvent polarity, indicating dipole changes within the ground excited state.

### Table 3

Good correlation with the  $\pi^*$  parameters defined by Kamlet and Taft <sup>[24]</sup> is 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  $\pi^*$  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 oriented parallel to the transition dipole and is moreover constant over the whole charge transfer band.

### Table 4

## Conclusion

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

All reactions were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying agents under dinitrogen. The synthesis of 5-formyl-5'-alkoxy-2,2'-bithiophenes<sup>[13]</sup> and complexes, *trans*-[Mo(N<sub>2</sub>)(dppe)<sub>2</sub>] and *trans*-[MoF(NNH<sub>2</sub>)(dppe)<sub>2</sub>]<sup>[17]</sup> have already been described.

The NMR spectra were obtained on a Varian Unity Plus Spectrometer at 300 MHz using the solvent peak as internal reference. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. UV-visible absorption spectra were obtained using a Shimadzu UV/2501PC spectrophotometer. High-resolution mass spectra (HRMS) were obtained with a GV AutoSpec spectrometer using an *m*-nitrobenzyl alcohol (NBA) matrix. Elemental analyses were performed

with a Leco CHNS-932 analyser. Voltammetric measurements were performed using a potentiostat/galvanostat (AUTOLAB /PSTAT 12 with low current module ECD from ECO-CHEMIE) and the data analysis processed by the General Purpose Electrochemical System software package (ECO-CHEMIE). Three electrode-two compartment cells equipped with vitreous carbon-disc working electrodes, a platinum-wire 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 mmol dm<sup>-3</sup> and 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>] was used as the supporting electrolyte in *N,N*-Dimethylformamide solvent. The potential was measured with respect to ferrocenium/ferrocene as an internal standard. Controlled-potential electrolyses were carried out in an H-type cell with a vitreous carbon working electrode as described previously.<sup>[12]</sup>

**General procedure for preparation of complexes 6-10.** The complex *trans* - [MoF(NNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>] (0.2 g, 0.19 mmol) was dissolved 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 solutions was reduced to *ca.* 5 ml and the precipitates were filtered off. These solids were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a pad of Celite. The solutions were evaporated to dryness and the solids obtained washed with cold THF (3 x 5 mL) then Et<sub>2</sub>O (2 x 3 mL) and dried *in vacuo* giving complexes **6-10** as coloured solids. In all cases, the solids thus obtained were crystallised from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O.

**6** – Pink solid. Yield 0.16 g, 73 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.4-2.8 (m, 8H, 2xPCH<sub>2</sub>CH<sub>2</sub>P), 3.4 (s, 3H, OCH<sub>3</sub>), 4.6 (s, 1H, N=CH), 6.8 - 7.4 (m, 42H, 40-*H* and 2-*H* of thienyl) ppm. <sup>31</sup>P-<sup>1</sup>H}RMN (121.7 MHz, CDCl<sub>3</sub>): δ = -100.3 (s, MoP) ppm. IR (KBr):  $\tilde{\nu}$  = 1550 (N=C) cm<sup>-1</sup>. HRMS (NBA): *m/z* = 1067.1968 [M]<sup>+</sup>; calcd. for C<sub>58</sub>H<sub>54</sub>FMoN<sub>2</sub>OP<sub>4</sub>S 1067.1945. C<sub>58</sub>H<sub>54</sub>BF<sub>5</sub>MoN<sub>2</sub>OP<sub>4</sub>S (1152.78): 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 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.4-2.7 (m, 8H, 2xPCH<sub>2</sub>CH<sub>2</sub>P), 3.6 (s, 3H, OCH<sub>3</sub>), 4.5 (s, 1H, N=CH), 6.8 - 7.4 (m, 44H, 40-*H* of phenyl and 4-*H* of bithienyl) ppm. <sup>31</sup>P-<sup>1</sup>H}RMN (121.7 MHz, CDCl<sub>3</sub>): δ = -100.1 (s, MoP) . IR (KBr):  $\tilde{\nu}$  = 1534 cm<sup>-1</sup> (N=C). HRMS (NBA): *m/z* = 1149.1816 [M]<sup>+</sup>; calcd. for C<sub>62</sub>H<sub>56</sub>FMoN<sub>2</sub>OP<sub>4</sub>S<sub>2</sub> 1149.1823. C<sub>62</sub>H<sub>56</sub>BF<sub>5</sub>MoN<sub>2</sub>OP<sub>4</sub>S<sub>2</sub> (1234.91): 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 %.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.6$  (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 2.4-2.7 (m, 8H,  $2\times\text{PCH}_2\text{CH}_2\text{P}$ ), 3.5 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.5 (s, 1H,  $\text{N}=\text{CH}$ ), 6.9 - 7.5 (m, 42H, 40-*H* of phenyl and 2-*H* of thienyl) ppm.  $^{31}\text{P}$ - $\{^1\text{H}\}$ RMN (121.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -100.2$  (s, MoP) ppm. IR (KBr):  $\tilde{\nu} = 1546\text{ cm}^{-1}$  ( $\text{N}=\text{C}$ ). HRMS (NBA):  $m/z = 1081.2118$   $[\text{M}]^+$ ; calcd. for  $\text{C}_{59}\text{H}_{56}\text{FMoN}_2\text{OP}_4\text{S}$  1081.2102.  $\text{C}_{59}\text{H}_{56}\text{BF}_5\text{MoN}_2\text{OP}_4\text{S}$  (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 %.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.8$  (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 2.4-2.7 (m, 8H,  $2\times\text{PCH}_2\text{CH}_2\text{P}$ ), 3.8 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.3 (s, 1H,  $\text{N}=\text{CH}$ ), 7.0 - 7.6 (m, 44H, 40-*H* of phenyl and 4-*H* of bithienyl) ppm.  $^{31}\text{P}$ - $\{^1\text{H}\}$ RMN (121.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -99.7$  (s, MoP) ppm. IR (KBr):  $\tilde{\nu} = 1515\text{ cm}^{-1}$  ( $\text{N}=\text{C}$ ). HRMS (NBA):  $m/z = 1163.1929$   $[\text{M}]^+$ ; calcd. for  $\text{C}_{63}\text{H}_{58}\text{FMoN}_2\text{OP}_4\text{S}_2$  1163.1979  $\text{C}_{63}\text{H}_{58}\text{BF}_5\text{MoN}_2\text{OP}_4\text{S}_2$  (1248.93): 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 %.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.5$  (d,  $J = 6.1$  Hz, 6H,  $\text{OCH}(\text{CH}_3)_2$ ), 2.3-2.7 (m, 8H,  $2\times\text{PCH}_2\text{CH}_2\text{P}$ ), 3.4 (m, 1H,  $\text{OCH}(\text{CH}_3)_2$ ), 4.2 (s, 1H,  $\text{N}=\text{CH}$ ), and 6.9 - 7.6 (m, 44H, 40-*H* of phenyl and 4-*H* of bithienyl) ppm.  $^{31}\text{P}$ - $\{^1\text{H}\}$ RMN (121.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -99.8$  (s, MoP) ppm. IR (KBr):  $\tilde{\nu} = 1519\text{ cm}^{-1}$  ( $\text{N}=\text{C}$ ). HRMS (NBA):  $m/z = 1177.2101$   $[\text{M}]^+$ ; calcd. for  $\text{C}_{64}\text{H}_{60}\text{FMoN}_2\text{OP}_4\text{S}_2$  1177.2136.  $\text{C}_{64}\text{H}_{60}\text{BF}_5\text{MoN}_2\text{OP}_4\text{S}_2$  (1262.96): 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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## CAPTIONS

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

<sup>a</sup> All measurements were recorded at 298 K in outgassed acetonitrile solutions with [NBu<sub>4</sub>][BF<sub>4</sub>] (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 V s<sup>-1</sup>. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted in volts vs. the ferrocene-ferrocenium couple ( $E_{1/2}(\text{fc}^+/\text{fc}) = 0.38 \text{ V/SCE}$ ). <sup>b</sup> Measured in acetonitrile.

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

<sup>a</sup> All measurements were recorded at 298 K in outgassed acetonitrile solutions with [NBu<sub>4</sub>][BF<sub>4</sub>] (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 V s<sup>-1</sup>. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted in volts vs. the ferrocenium-ferrocene-couple ( $E_{1/2}(\text{fc}^+/\text{fc}) = 0.38 \text{ V/SCE}$ ). <sup>b</sup> Measured in acetonitrile.

**Figure 1.** Cyclic voltammogram of *trans*-[FMo{NN=CH(5'-OEt-2,2'-bithienyl)}(dppe)<sub>2</sub>][BF<sub>4</sub>] (**9**) in DMF-0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>] at a vitreous carbon electrode (area = 0.049 cm<sup>2</sup>). Scan rate 100 mV s<sup>-1</sup>, concentration of complex 2.3 mmol dm<sup>-3</sup>.

**Figure 2.** UV-visible spectra of 2-formyl-5-methoxythiophene (**1**) and *trans*-[FMo{NN=CH(5'-methoxythienyl)}(dppe)<sub>2</sub>][BF<sub>4</sub>] (**6**) were recorded in acetonitrile, demonstrating the effect of the Mo part on the absorption maxima between 300 and 700 nm.

**Table 3.** Solvatochromic data [ $\lambda_{\text{max}}$  (nm) and  $\tilde{\nu}_0$  ( $\text{cm}^{-1}$ ) of the charge-transfer band] for complexes **6-10**, in selected solvents in comparison with  $\pi^*$  values by Kamlet and Taft.<sup>[24]</sup>

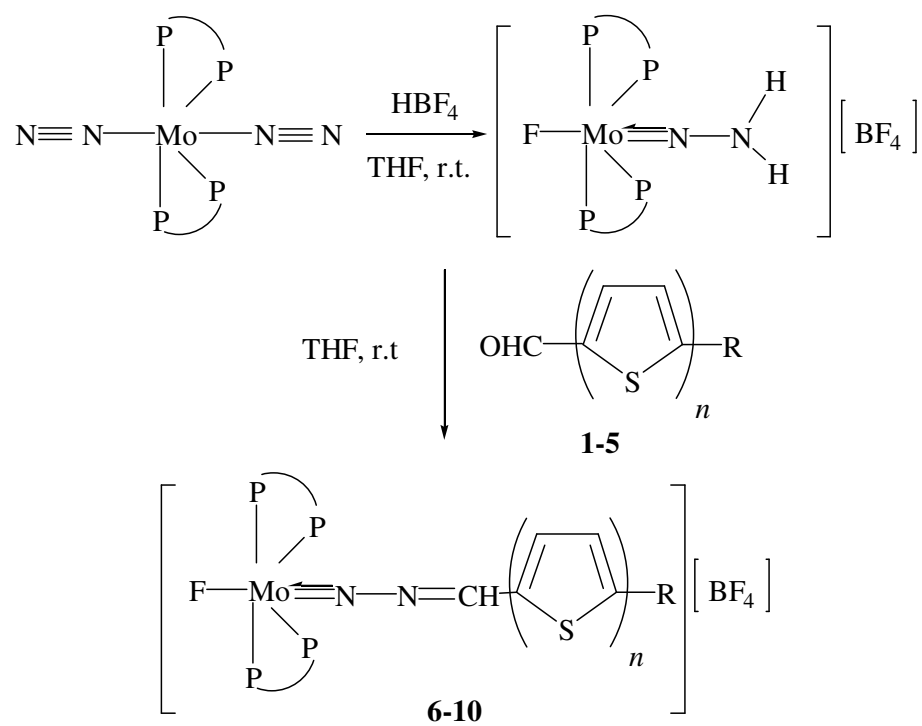
**Table 4.** Correlation of UV-Vis absorption maxima of complexes **6-10** and solvent parameter  $\pi^*$ <sup>a</sup>

<sup>a</sup> Applied solvents ( $\pi^*$  value): (0.58), acetone (0.71), acetonitrile (0.75), dichloromethane (0.82) and dimethylsulfoxide (1.0).

<sup>b</sup> Intercept, slope, and correlation  $r$  of the linear solvation energy relationship, according to equation  $\nu_{\text{max}} = \nu_0 + s\pi^*$ .

## Schemes

Scheme 1



R	<i>n</i>	Thiophenic or bithiophenic group	Complex	Yield [%]
OMe	1	<b>1</b>	<b>6</b>	73
OMe	2	<b>2</b>	<b>7</b>	77
OEt	1	<b>3</b>	<b>8</b>	67
OEt	2	<b>4</b>	<b>9</b>	78
O( <i>i</i> Pr)	2	<b>5</b>	<b>10</b>	65

## TABLES

### TABLE 1

Compound	R	<i>n</i>	Electrochemical data <sup>a</sup>		Electronic spectral data <sup>b</sup>	
			Reductions	Oxidations	$\lambda_{\max}$ [nm]	$10^{-3}\epsilon$ [dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> ]
			-E <sub>pr</sub> [V]	E <sub>pa</sub> [V]		
<b>1</b>	OMe	1	2.30	0.86	310	24.7
<b>2</b>	OMe	2	2.00	0.76	362	16.3
<b>3</b>	OEt	1	2.34	0.82	316	21.2
<b>4</b>	OEt	2	2.08	0.74	391	24.5
<b>5</b>	O(Pr- <i>i</i> )	2	2.14	0.73	393	23.8

### TABLE 2

Complex	R	<i>n</i>	Electrochemical data <sup>a</sup>				Electronic spectral data <sup>b</sup>	
			Reduction	Oxidations			$\lambda_{\max}$ [nm]	$10^{-3}\epsilon$ [dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> ]
			-E <sub>c1/2</sub> [V]	E <sub>a1/2</sub> [V]	E <sub>pa1</sub> [V]	E <sub>pa2</sub> [V]		
<b>6</b>	OMe	1	1.45	0.24	0.47	0.87	469	17.2
<b>7</b>	OMe	2	1.36	0.28	0.53	0.76	482	17.4
<b>8</b>	OEt	1	1.50	0.20	0.42	0.83	474	18.1
<b>9</b>	OEt	2	1.40	0.24	0.50	0.74	497	16.7
<b>10</b>	O(Pr- <i>i</i> )	2	1.43	0.20	0.47	0.74	496	19.3

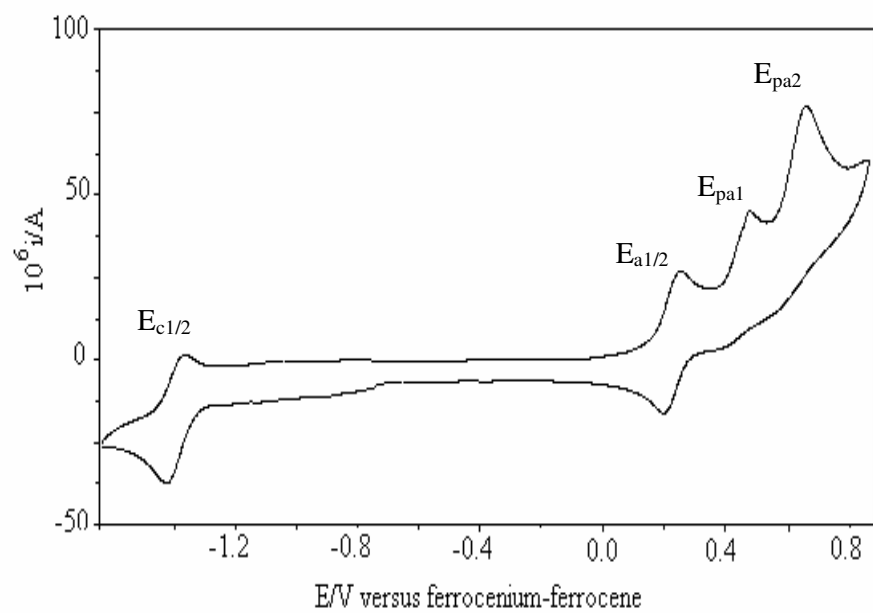
**TABLE 3**

Complex	Solvent ( $\pi^*$ )									
	THF (0.58)		Acetone (0.71)		Acetonitrile (0.75)		CH <sub>2</sub> Cl <sub>2</sub> (0.82)		DMSO (0.88)	
	$\lambda_{\max}$	$\tilde{\nu}_{\max}$	$\lambda_{\max}$	$\tilde{\nu}_{\max}$	$\lambda_{\max}$	$\tilde{\nu}_{\max}$	$\lambda_{\max}$	$\tilde{\nu}_{\max}$	$\lambda_{\max}$	$\tilde{\nu}_{\max}$
<b>6</b>	466	21,459	468	21,413	469	21,322	471	21,231	474	21,097
<b>7</b>	479	20,877	481	20,790	482	20,747	485	20,619	488	20,492
<b>8</b>	479	20,877	482	20,747	484	20,661	487	20,534	490	20,408
<b>9</b>	493	20,284	495	20,202	497	20,121	501	19,960	505	19,802
<b>10</b>	491	20,366	494	20,243	496	20,161	499	20,040	502	19,920

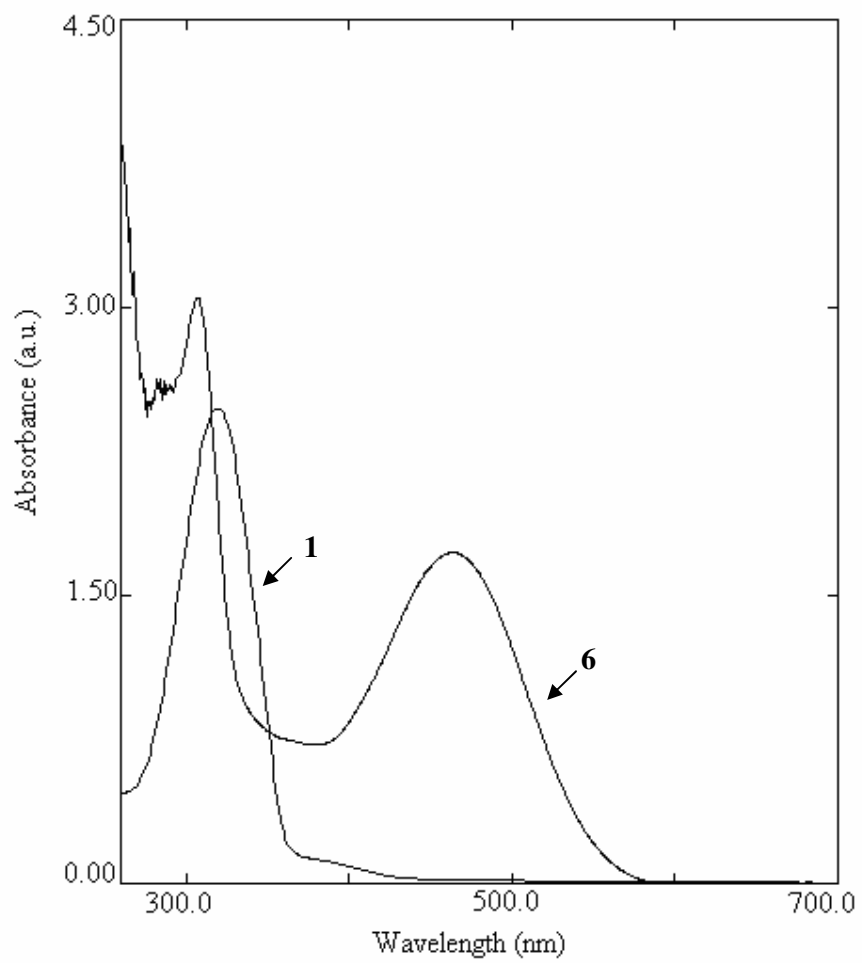
**TABLE 4**

Complexes	$\tilde{\nu}_0^b$ [cm <sup>-1</sup> ]	Regression analysis $s^b$	$r^b$
<b>6</b>	22,013	-917.62	0.9760
<b>7</b>	21,448	-962.61	0.9843
<b>8</b>	21,590	-1,158.20	0.9814
<b>9</b>	20,989	-1,196.40	0.9863
<b>10</b>	20,997	-1,101.80	0.9760

FIGURE 1



**FIGURE 2**



## Graphical Abstract

