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# Molybdenum Complexes Bearing (Bi)thienyl- or Arylthienyl-Substituted π-Conjugated Spacers: Synthesis, Electrochemical, Spectroscopic and Nonlinear Optical Properties

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A series of complexes *trans*-[FMo(N=NCHL)(dppe)$_2$][BF$_4$] {L = (bi)thienyl or arylthienyl}, were synthesized and fully characterized by $^1$H, $^{13}$C, $^{31}$P NMR, IR and UV/Vis spectroscopy. The electronic spectra and electrochemical behavior of the complexes were investigated. The electronic absorption spectra of these complexes display a broad low-energy band in the visible region attributable to metal-to-ligand charge-transfer (MLCT) transitions. The electron-conjugated effect with the heterocyclic nucleus led to a notable improvement of visible light absorption and marked changes in the electrochemical behavior. The hyperpolarizabilities β of the synthesized compounds were evaluated using the hyper-Rayleigh scattering technique.

## Introduction

Extensive theoretical and experimental efforts have been directed to the design of new molecular materials with large second-order nonlinear optical (NLO) responses, motivated in part by their potential applications in low-cost, high-performance photonic, and electrooptical devices.[1–4] The exploitation of organometallic chemistry for the synthesis of new compounds with nonlinear optical (NLO) properties has been mainly driven by the optical devices technology.[5–7] The significant work already published in this area is in agreement with the general understanding that second-order nonlinearities are strongly related to asymmetric push–pull systems, both in organic and organometallic molecular materials.[8–15]

The thiophene moiety has been studied as chromophore both in organic[16–21] and organometallic[22–29] materials for NLO. Compounds incorporating thiophene are currently recognized to exhibit enhanced second-order polarizabilities in comparison to π-systems with phenylene bridges, mainly due to thiophene's lower delocalization energy, leading to a more effective conjugation. These systems can be obtained by combining a π-conjugated chain with electron donor and/or acceptor groups (D-π-A or push–pull systems) in which metal centers can behave either as acceptor or donor group simply by varying the metal and/or its oxidation state. In the case of metallo-organic compounds, the metal centre can be bound to a highly polarizable conjugated backbone, acting as an electron releasing or withdrawing group. Consequently, strong charge-transfer (CT) transitions can occur, leading to high molecular first hyperpolarizabilities ($\beta$). Moreover, the position of these CT bands, which usually appear in the visible region, can be tuned by variation of the coligands and/or the metal itself, to optimize the hyperpolarizability through (near) resonant enhancement. Recent theoretical work on the stability, redox and NLO properties of arylimido hexamolybdate derivatives[30,31] has concluded that electron donor-acceptor polyoxometalate derivatives have the potential to be highly efficient NLO materials.[32,33]

Transition metal complexes of the general type *trans*-[MX(NNR)(dppe)$_2$]$^+$ [M = Mo or W; X = halide: dppe = 1,2-bis(di-arylphosphanyl)ethane in which R is a heterocyclic group, are particularly attractive due to its conjugated structure which includes the central metal atom and the robust square-planar {M(dppe)$_2$} assembly.[23,34]

As part of our continuing interest in developing organic and organometallic chromophores for NLO applications[18–21,23,24] we decided to synthesize new metal transition complexes bearing (bi)thiophenes or arylthiophenes as spacers in order to evaluate the effect of π-conjugated heterocyclic bridge on the electronic and optical properties of the corresponding organometallic complexes. In this report, we evaluate the electrochemical, spectroscopic and NLO properties of the newly synthesized molybdenum complexes.

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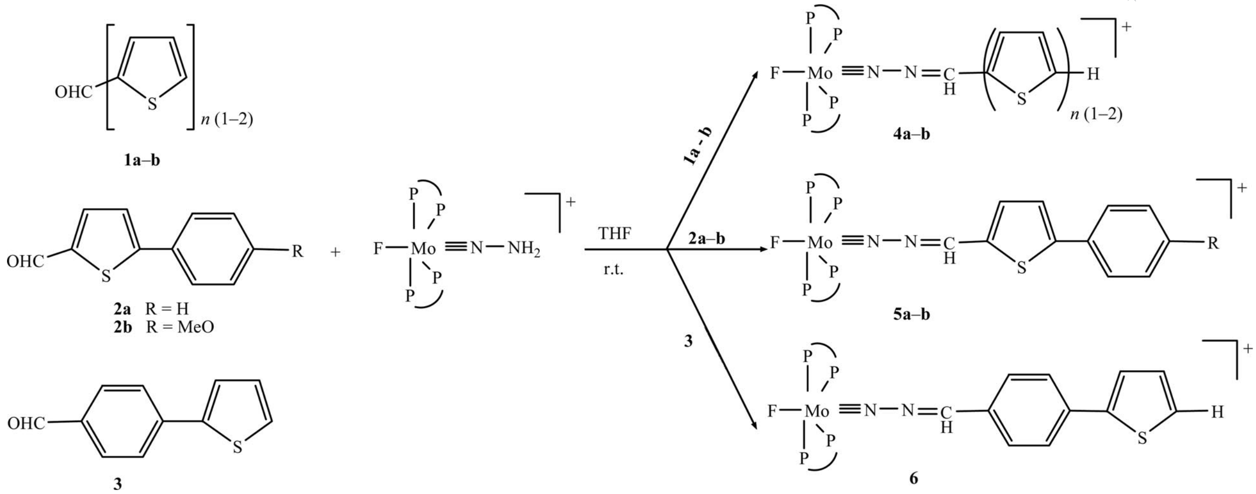


Scheme 1. Synthesis of the new complexes *trans*-[FMo{N=NCH(heterocycle)}(dppe)$_2$][BF$_4$] **4**–**6**.

## Results and Discussion

### I. Syntheses of the Molybdenum Complexes 4–6

In order to compare the effect of the electronic nature and the length of the π-conjugated bridge on the optical and electronic properties of molybdenum complexes **4**–**6**, formyl-(bi)thiophenes **1** and formyl-arylthiophenes **2**–**3** were used as precursors of complexes **4**–**6**. Precursors **1a**–**b** and **2** were commercially available and the synthesis of formyl-arylthiophenes **2b** and **3** was described elsewhere.[35]

The method to make the complexes with carbon–nitrogen bonds involves the initial conversion of *trans*-[M(N$_2$)$_2$(dppe)$_2$] into the hydrazido(2–) complexes, *trans*-[MF(NNH$_2$)(dppe)$_2$][BF$_4$].[36,37] This complex is susceptible to electrophilic attack at the terminal nitrogen atom therefore they can serve as key intermediate in the preparation of organo-nitrogen complexes by subsequent reactions with organic carbonyl compounds.[23,38] Thus, the condensation reaction of *trans*-[MF(NNH$_2$)(dppe)$_2$][BF$_4$] with a slight excess of the formyl-(bi)thiophenes **1**, and formyl-arylthiophenes **2**–**3**, gave the molybdenum complexes **4a**–**b**, **5a**–**b** and **6**, respectively (Scheme 1).

Reactions were carried out at room temperature, stirring overnight, under inert atmosphere. Compounds were recrystallized from dichloromethane/diethyl ether, affording crystalline pink or orange products. All compounds were stable to air and moisture, either in the solid state or in solution and were obtained in good to excellent yields (70–90%). The formulation is supported by FT-IR and $^1$H, $^{31}$P NMR spectroscopic data, high-resolution mass spectra (HRMS) and by elemental analysis.

The IR spectra of complexes **4a**–**b**, **5a**–**b** and **6** are dominated by the characteristic bands of diphenylphosphane ligands (1484, 1435, 742 and 691 cm$^{-1}$) and the ν(C=N) stretching vibrations about 1558–1580 cm$^{-1}$.[23,34,37] The shifts observed on ν(C=N) stretching has been attributed to π-backdonation, due to π bonding between the d orbitals of the metal and the π* orbital of the heterocyclic imide group, which leads to a variation in C=N bond order.[38] Accordingly, the highest shift of 14 cm$^{-1}$ was found for **5b** compared to **5a** which corresponds to the complex having the arylthienyl moiety functionalized with the methoxy group.

As expected, the $^1$H NMR spectra of complexes **4a**–**b**, **5a**–**b** and **6** shows the signals of each proton of the (bi)-thienyl and arylthienyl moieties and diphenylphosphane ligands. $^1$H NMR resonances for the (diarylphosphanyl)ethane group are in the characteristic range of monocationic molybdenum complexes. The effect of coordination on the heterocyclic ligands is observed through the shielding of the first thiophene unit (**4a**–**b** and **5a**–**b**) or on the aryl ring protons **6**, indicating an electronic flow towards the heteroaromatic ligand due to π-backdonation involving the metal centre. This effect is very pronounced in these complexes with dppe, showing the better σ-donor ability of this coligand, with shieldings on the aromatic protons of the ligands ($\delta_{\text{complexe}} - \delta_{\text{free ligand}}$ about –0.3 ppm), this indicating that the electronic flow is extended throughout the entire π-system.

$^{31}$P{$^1$H} NMR spectroscopic data of the complexes showed a single sharp signal for the phosphane coligands (dppe) revealing the equivalency of the two phosphorus atoms, and an expected deshielding upon coordination, in accordance with its σ donor character.

### II. Electrochemical Studies

In order to get more insight on the electronic properties of the compounds **1**–**3** and **4**–**6**, the electrochemical behavior of molybdenum compounds and the free sulfur heterocyclic ligands were studied by cyclic voltammetry in acetonitrile, between the limits imposed by the solvents.

Relevant data for the redox changes exhibited by the precursors **1**–**3** are summarized in Table 1. The electrochemical behavior of these compounds is characterized by one irreversible oxidation which can be attributed to the formation of the radical cation of the heterocyclic part, with $E_{\text{pa}}$ ranging from 0.67 V to 0.85 V in acetonitrile, without any cathodic counterpart. The oxidation process of the bithienyl group (**1b**) is shifted to less positive potentials than those of the thienyl group (**1a**). This fact can be explained by the stabilisation of the cation radical due to its higher delocalisation on the bithienyl moiety. The influence of the incorporation of arylthiophene moieties in push-pull compounds on oxidation process is low. After few sweeps, some additional oxidation and reduction broad waves were observed for chromophores **1a**, **1b**, and **2b**, attributed to the product deposition observed at the carbon electrode surface, this being compatible with the expected potential-induced polymerization of thiophenes.[39]

Table 1. Electrochemical and electronic spectroscopic data for the (bi)thienyl and arylthienyl ligands **1**–**3**.

| Formyl precursor | Electrochemical data[a] Reduction $-E_{pc}$[V] | Oxidation $E_{pa}$[V] | Electronic spectroscopic data[b] $\lambda_{max}$ [nm] | $10^{-3}$ $\varepsilon$ [$M^{-1}$ $cm^{-1}$] |
|---|---|---|---|---|
| **1a** | – | 0.85 | 245 | 20.6 |
| **1b** | 2.05 | 0.71 | 351 | 17.1 |
| **2a** | 2.00 | 0.75 | 332 | 16.7 |
| **2b** | 2.10 | 0.67 | 353 | 19.5 |
| **3** | 1.97 | 0.78 | 324 | 21.7 |

[a] All measurements were recorded at 298 K in outgassed acetonitrile solutions with $[NBu_4][BF_4]$ (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 V s$^{-1}$. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted in volts vs. the ferrocene/ferrocenium couple [$E_{1/2}(fc^+/fc)$ = 0.38 V/SCE]. [b] Measured in acetonitrile.

At low potentials (less than –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 arylthiophene and its delocalisation on the heterocyclic part is more difficult.

Cyclic voltammetry studies revealed that the complexes undergo reversible oxidation in solution, assigned to the $Mo^{IV/V}$ couple [$i_{pc}/i_{pa} \approx 1$, $\Delta E_p(Mo^{IV/V}) \approx \Delta E_p$(ferrocene/ferrocenium)]. Relevant data for the redox changes exhibited by the complexes **4**–**6** are summarized in Table 2. Comparison of values obtained for complexes **1**–**3** and **4**–**6** with the parent complex *trans*-$[FMo(NNH_2)(dppe)_2][BF_4]$ (0.34 V vs. fc$^+$/fc)[23] shows that the combination of several factors such as the different electronic nature of the heterocyclic spacer: (bi)thiophene or arylthiophene, the length of the heterocyclic bridge and the electronic donor nature of the ligands thoroughly stabilises $Mo^V$.

This fact can be explained by metal to heterocyclic group $\pi^*$ orbital backdonation via the hydrazido ligand. This backdonation increases in the case of an arylthienyl conjugated bridge, which contributes to the stabilisation of the metal-centred HOMO orbital. For both type of complexes (bearing a (bi)thienyl $\pi$-conjugated bridges **4a**–**b** or arylthienyl spacers **5a**–**b**), the results suggests a $\pi$-conjugated system between the metallic group and the (bi)thienyl or arylthienyl moieties. The electrochemical behaviour of the molybdenum complexes **5a** and **6** indicate that the different position of linkage of the arylthienyl spacer to the molybdenum complex (through the thiophene heterocycle **5b**) or through the aryl ring **6**, has little influence on the electronic delocalization from the heterocyclic ligand to the metal.

The reduction of the complex occurs in a quasi-reversible one-electron process ($\Delta E$p = 150 mV). For compound **4b** with a bithiophenic linker the reduction potentials are shifted to more cathodic values compared to **4a**.

Complexes bearing arylthienyl linkers do not show significant changes in their reduction potentials. In the arylthiophene spacers the corresponding stabilisation of their LUMO ($\pi^*$) orbital does not correspond to an electron-donor effect of these heterocyclic bridges, but to a better delocalisation of the injected electrons into the ligand via the imino bridge.

For the study of second-order nonlinear optics, it is relevant to evaluate the HOMO–LUMO gap, expressed by the difference between the first oxidation and reduction potentials.[40] As is to be expected, the data show that the HOMO–LUMO gap depends both on the electronic nature and the length of the heterocyclic spacer.

## III. UV/Vis and Solvatochromic Studies

The optical absorption spectra of all formyl precursors **1**–**3** and the synthesized new complexes **4**–**6** were recorded in ca. $5 \times 10^{-5}$mol dm$^{-3}$ in acetonitrile solutions. Electronic absorption spectra of all complexes **4a**–**b**, **5a**–**b** and **6** bearing heterocyclic groups showed an intense lowest energy

Table 2. UV/vis absorption and electrochemical data for complexes **4a**–**b** and **5a**–**b** and **6**.

| Entry | Complex | Electrochemical data[a] Reduction $-E_{1/2}$ [V] | Oxidations $^1E_{1/2}$ [V] | $^2E_{pa}$ [V] | Band gap [eV][b] | Electronic spectroscopic data[c] $\lambda_{max}$ [nm] | $10^{-3}$ $\varepsilon$ [$M^{-1}$ $cm^{-1}$] |
|---|---|---|---|---|---|---|---|
| 1 | **4a** | 1.41 | 0.39 | 0.71 | 1.80 | 457 | 14.6 |
| 2 | **4b** | 1.32 | 0.35 | 0.65 | 1.67 | 484 | 18.2 |
| 3 | **5a** | 1.36 | 0.37 | 0.62 | 1.73 | 482 | 12.3 |
| 4 | **5b** | 1.38 | 0.25 | 0.56 | 1.63 | 486 | 16.1 |
| 5 | **6** | 1.37 | 0.38 | 0.61 | 1.75 | 480 | 10.5 |

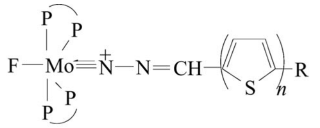
[a] All measurements were recorded at 298 K in outgassed acetonitrile solutions with $[NBu_4][BF_4]$ (0.2 M) as supporting electrolyte at a carbon working electrode with a scan rate of 0.1 V s$^{-1}$. Ferrocene was added as an internal standard at the end of each measurement, potentials were converted in volts vs. the ferrocenium-ferrocene-couple [$E_{1/2}$ (fc$^+$/fc) = 0.38 V/SCE]. [b] $E_{HOMO} = 4.39 + {}^1E_{1/2}$ [eV] and $E_{LUMO} = E_{1/2} + 4.39$ [eV]. [c] Measured in acetonitrile.

charge-transfer absorption band in the visible region (Table 2).

As expected, for the ligands **1**–**3**, the π–π* transition band depends on the length and on the electronic nature of the π-conjugated spacer (Table 1).

The position of this band was strongly influenced by the structure of the compounds, for example by the length of the π conjugated bridge and by the electronic nature of the groups (H or methoxy), substituted on the arylthienyl moiety of the conjugated system (Table 2).

The peak of maximum absorption for the bithienyl complex **4b** compared to the thienyl compound **4a** was shifted to a longer wavelength (27.5 nm) due to the increase of the number of thiophene units, as expected from the increase in conjugation, which reduces the gap between the highest occupied molecular orbital (HOMO) and the LUMO (Table 2). Similar results were obtained for the UV/Vis. study of the alkoxy-(bi)thiophenic Mo complexes **7**–**9** previously reported by us (Figure 1).[23]



| R | *n* | Complex |
|---|---|---|
| OMe | 1 | **7a** |
| OMe | 2 | **7b** |
| OEt | 1 | **8a** |
| OEt | 2 | **8b** |
| O(*i*Pr) | 2 | **9** |

Figure 1. Structures of complexes **7**–**9**.[23]

Remarkable differences in energy occur upon conversion of formyl ligands **1**–**3** to complexes **3**–**6**. For example, formyl-bithiophene **1b** ($\lambda_{max}$ = 351 nm) is shifted 133 nm (complex **4b**, $\lambda_{max}$ = 484 nm) (see Tables 1 and 2, Figure 2).

The intramolecular charge-transfer process, which is originated in the Mo part and is propagated through the π-conjugated spacer [hydrazido(–2)], gives rise to a considerable bathochromic shift of the (bi)thienyl and arylthienyl transitions. Similar tendencies were observed for complexes of molybdenum bearing alkoxy-(bi)thienyl ligands.[23]

It has long been recognized that nonlinear optical (NLO) activity of chromophores is determined not only by donor-acceptor strength but more subtly by conjugated electron relays. This can be understood from the difference in relay activities between typical moieties such as polyene and oligophenylene or oligothiophene which bear the same donor–acceptor pair and the same conjugation length; a more pronounced red-shift (in a given solvent), indicative of increased electron transmission, is commonly observed with polyenes in the low energy absorption maximum $\lambda_{max}$ as compared to the oligophenylenes and oligothiophenes. Such a tendency is intensified with an increase of solvent polarity. Positive solvatochomism has been regarded as an important indicator of the potential molecular nonlinearity ($\mu\beta$) of NLO chromophores.[41] Previous studies have demonstrated that donor-acceptor substituted oligothiophenes exhibit a positive solvatochromism.[18–19,21] In order to investigate whether complexes **4**–**6** exhibit a positive solvatochromism, we carried out a study of the absorption spectra of compounds **4a**–**b**, **5a**–**b** and **6** in four polar solvents (ethanol, tetrahydrofuran, acetonitrile and dimethylformamide) of different solvation character (Table 3). Due to the insolubility of these complexes it was not possible to extend this study using apolar solvents. The wavelength maxima $\lambda_{max}$ of compounds **4**–**6** are listed in Table 3 and were compared with π* values for each solvent, determined by Kamlet et al.[42] Complexes **4**–**6** exhibited positive solvatochromism with respect to their CT absorption band, i.e. the position of the absorption maximum shifted to longer wavelengths as the polarity of the solvent increased due to a greater stabilization of the excited state relative to the ground state with an increase in the polarity of the solvent. Moreover, compound **5b** ($\Delta\tilde{\nu}_{max}$ = 484 cm$^{-1}$) showed the longest shifts in wavenumber maxima.

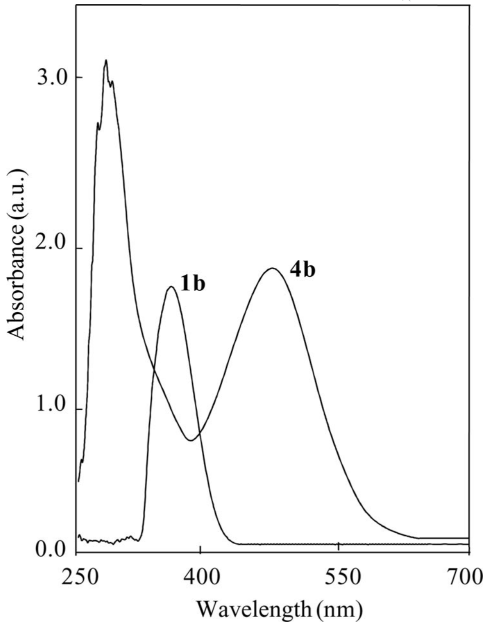


Figure 2. UV/Vis spectra of formyl-bithiophene (**1b**) and *trans*-{FMo[NN = CH(bithienyl)](dppe)$_2$}[BF$_4$] (**4b**) recorded in acetonitrile.

Table 3. Solvatochromic data ($\lambda_{max}$ [nm] of the charge-transfer band) for complexes **4a**–**b** and **5a**–**b** and **6** in various solvents with π* values by Kamlet and Taft.[42]

| Solvent (π*) | Complex | | | | |
|---|---|---|---|---|---|
| | **4a** | **4b** | **5a** | **5b** | **6** |
| | $\lambda_{max}$ | $\lambda_{max}$ | $\lambda_{max}$ | $\lambda_{max}$ | $\lambda_{max}$ |
| Ethanol (0.54) | 454 | 481 | 479 | 482 | 477 |
| THF (0.58) | 456 | 483 | 481 | 484 | 479 |
| Acetonitrile (0.75) | 457 | 484 | 482 | 486 | 480 |
| DMF (0.82) | 461 | 487 | 485 | 491 | 483 |
| DMSO (1.00) | 463 | 489 | 486 | 493 | 485 |

Table 4. UV/Vis absorptions, $\beta$ values, $\beta_0$ values for *p*NA and for complexes **4**–**6** and for **7**–**9**.

| | R | *n* | $\lambda_{max}$ [nm][a] | $\beta/10^{-30}$ [esu][b] | $\beta_0/10^{-30}$ [esu][c] | Comp.[23] | R | *n* | $\lambda_{max}$ [nm][a] | $\beta/10^{-30}$ [esu][b] | $\beta_0/10^{-30}$ [esu][c] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **4a** | H | 1 | 455 | 50 | 11 | **7a** | MeO | 1 | 467 | 110 | 20 |
| **4b** | H | 2 | 484 | 101 | 14 | **7b** | MeO | 2 | 489 | 147 | 18 |
| **5a** | H | – | 483 | 89 | 12 | **8a** | EtO | 1 | 483 | 125 | 17 |
| **5b** | MeO | – | 486 | 115 | 15 | **8b** | EtO | 2 | 499 | 173 | 16 |
| **6** | H | – | 480 | 74 | 11 | **9** | O(*i*OPr) | 2 | 497 | 150 | 15 |
| *p*NA | – | – | 352 | 23[15,49] | 8 | – | – | – | – | – | – |

[a] Experimental hyperpolarizabilities and spectroscopic data measured in chloroform solutions. [b] All the compounds are transparent at the 1064 nm fundamental wavelength. [c] Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta[1 - (\lambda_{max}/1064)^2][1 - (\lambda_{max}/532)^2]$; damping factors not included 1064 nm.[43,44]

### IV. Non-Linear Optical Study of Molybdenum Complexes 4–6

We have used the hyper-Rayleigh scattering (HRS) method to measure the first hyperpolarizability $\beta$ of the molybdenum complexes **4a**–**b** and **5a**–**b** and **6**, using the 1064 nm fundamental wavelength of a Nd:YAG laser. We accounted for the possible fluorescence contributions subsequent to two photon absorption of the incident laser light, by using interference filters in the detection arm of our set-up. The signals transmitted through two different interference filters both centered at 532 nm, but with different bandwidths were measured. The difference between these signals allows us to estimate the fluorescence contribution to the measured signal as it was explained in more detail previously.[21] Table 4 shows the measured values of $\beta$ together with the lowest energy absorption maximum of each complex. We have used the standard two-level model that ignores damping to estimate the static second-order hyperpolarizability $\beta_0$[43,44] the results being included in Table 4. Due to the simplicity of the model, these extrapolated $\beta_0$ values should be treated with some caution.

Earlier we have reported the synthesis and the characterization of electrochemical, spectroscopic and solvatochromic properties of alkoxy-(bi)thiophenic molybdenum complexes **7**–**9**. In order to compare these Mo complexes with the recent (bi)thienyl and arylthienyl derivatives described in this article we decided also to evaluate the second order hyperpolarizability of these compounds.

From Table 4 it is obvious that the increase of the donor strength of the group substituted on the arylthiophenic (**5a**–**b**) or bithiophenic moieties (**4b** and **8b**) resulted both in red-shifted absorption maxima and enhanced $\beta$ values for complexes **5b** (R = MeO) and **8b** (R = EtO), in comparison to derivatives **5a** and **4b** for which R = H.

Noteworthy is also the effect of the length of the π-conjugated bridge on the $\beta$ values for the complexes bearing a thienyl spacer (e.g. **4a**, $\beta = 50 \times 10^{-30}$ esu) compared to complexes having a bithienyl conjugated bridge (e.g. **4b**, $\beta = 101 \times 10^{-30}$ esu).

On the other hand, comparison of the $\beta$ values for compounds **5a** ($\beta = 89 \times 10^{-30}$ esu) and **6** ($\beta = 74 \times 10^{-30}$ esu), showed that complexes linked to the Mo moiety through the aryl ring of the arylthienyl system have smaller nonlinearities than derivatives linked through the thiophene ring (Table 4). Thus the electronic nature of the spacer can either enhance or decrease the overall molecular nonlinearity of the system. This suggests that the arylthienyl moiety does not simply function as a conjugated segment, but also plays the role of a structural unit, which affects the overall electron-transfer properties of the system. While the aromaticity of heteroaromatics affects the electron transfer between donor and acceptor groups, the electron-excessive or electron-deficient nature of the heterocyclic ring systems may also play a major role in determining the overall electron-donating and accepting ability of the substituents: electron-rich heterocycles such as thiophene can act as auxiliary donors.[45] The arylthienyl moiety will act not only as a spacer but also as an auxiliary donor. These findings are in accordance with our recent work[19,46–48] in which we concluded that the increase or decrease of the molecular nonlinear activity of heteroaromatic systems depends not only on the electronic nature of the (hetero)aromatic rings but also on the position of substitution of the donor or acceptor groups on these systems.

## Conclusions

New molybdenum complexes containing thienyl or arylthienyl spacers have been synthesized and fully characterized. The electrochemical and spectroscopic data show that the increase of the length and the nature of the π-conjugated heterocyclic bridge and the electronic nature of the group that substitutes the thienyl or arylthienyl moieties have an effect on the electronic delocalization of the complexes.

The hyperpolarizability data determined by hyper-Rayleigh scattering showed that, the nonlinear optical response is dependent on the type of the π-conjugated bridge and the group (hydrogen or methoxy) that is substituted on the arylthienyl moieties. Overall the complexes have good molecular nonlinearities as their values are 2–5 times higher than the molecule *p*NA, a well-known standard. The combined results from our solvatochromic, electrochemical and nonlinear optical studies, suggest that the new compounds could be strong candidates for the applications that exploit materials with good nonlinear properties.

## Experimental Section

**General Procedures:** All the experiments were carried out under dinitrogen atmosphere using standard Schlenk techniques. All solvents were dried using standard methods.[50] Starting materials were prepared following the methods described in the literature: *trans*-[$Mo(N_2)(dppe)_2$] and *trans*-[$MoF(NNH_2)(dppe)_2$].[51,52] The synthesis of the formylated precursors are described elsewhere.[35]

The NMR spectra were obtained on a Varian Unity Plus Spectrometer at 300 MHz using the solvent peak as internal reference. The $^1$H chemical shifts are reported as δ values (ppm) downfield from internal $Me_4Si$ and the $^{31}$P NMR spectra are reported in ppm downfield from external standard $H_3PO4$ 85%. Solid state IR spectra were taken on a Perkin–Elmer 1600 FTIR spectrophotometer with KBr pellets. UV/Vis absorption spectra were obtained at room temperature on 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.

**Synthesis of the Complexes**

**General Procedure:** The complex *trans*-[$MoF(NNH_2)(dppe)_2$][$BF_4$] (0.25 g, 0.25 mmol) was dissolved in THF (25 mL) at room temperature. The ligands were added in a slight excess (0.28 mmol) to the solution which was stirred for 24 h under inert atmosphere. The volume of the solutions was reduced to ca. 5 mL and the precipitates were filtered off. These solids were dissolved in $CH_2Cl_2$ and filtered through a pad of Celite. The solutions were evaporated to dryness and the solids obtained washed with cold THF (3 × 5 mL) then $Et_2O$ (2 × 3 mL) and dried in vacuo giving complexes **4**–**6** as coloured solids. In all cases, the solids thus obtained were crystallised from $CH_2Cl_2/Et_2O$ or $CH_2Cl_2$/*n*-hexane.

**4a:** Pink solid. Recrystallized from $CH_2Cl_2/Et_2O$; yield 0.19 g, 67%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.6–2.8 (m, 8 H, 2× $PCH_2CH_2P$), 4.2 (s, 1 H, N=C*H*), 7.0–7.2 (m, 24 H, 24-*H* of phenyl), 7.4–7.6 (m, 19 H, 16-*H* of phenyl and 3-*H* of thienyl) ppm. $^{31}P\{^1H\}$NMR (121.7 MHz, $CDCl_3$): $\delta$ = –98.2 (s, MoP) ppm. IR (KBr): $\tilde{\nu}$ = 1580 (N=C) cm$^{-1}$. HRMS (NBA): *m*/*z* = 1037.1821 [M]$^+$; calcd. for $C_{57}H_{52}FMoN_2P_4S$ 1037.1834. $C_{57}H_{52}BF_5MoN_2P_4S$ (1122.75): calcd. C 60.98, H 4.67, N 2.50, S 2.86; found C 60.65, H 4.81, N 2.43, S 2.81.

**4b:** Pink solid. Recrystallized from $CH_2Cl_2/Et_2O$; yield 0.23 g, 76%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.4–2.7 (m, 8 H, 2× $PCH_2CH_2P$), 4.3 (s, 1 H, N=C*H*), 6.9–7.0 (m, 26 H, 24-*H* of phenyl and 2-*H* of bithienyl), 7.3–7.6 (m, 19 H, 16-*H* of phenyl and 3-*H* of bithienyl), ppm. $^{31}P\{^1H\}$NMR (121.7 MHz, $CDCl_3$): $\delta$ = –99.4 (s, MoP) ppm. IR (KBr): $\tilde{\nu}$ = 1566 (N=C) cm$^{-1}$. HRMS (NBA): *m*/*z* = 1119.1708 [M]$^+$; calcd. for $C_{61}H_{54}FMoN_2P_4S_2$ 1119.1711. $C_{61}H_{54}BF_5MoN_2P_4S_2$ (1204.88): calcd. C 60.54, H 4.46, N 2.27, S 5.26; found C 60.81, H 4.52, N 2.33, S 5.32.

**5a:** Orange solid. Recrystallized from $CH_2Cl_2$/*n*-hexane; yield 0.17 g, 58%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.5–2.8 (m, 8 H, 2× $PCH_2CH_2P$), 4.4 (s, 1 H, N=C*H*), 7.0–7.2 (m, 26 H, 24-*H* of phenyl and 2-*H* of thienyl), 7.4–7.7 (m, 21 H, 16-*H* of phenyl and 5-*H* aryl) ppm. $^{31}P\{^1H\}$NMR (121.7 MHz, $CDCl_3$): $\delta$ = –98.9 (s, MoP) ppm. IR (KBr): $\tilde{\nu}$ = 1571 (N=C) cm$^{-1}$. HRMS (NBA): *m*/*z* = 1113.2144 [M]$^+$; calcd. for $C_{63}H_{56}FMoN_2P_4S$ 1113.2147. $C_{63}H_{56}BF_5MoN_2P_4S$ (1198.85): calcd. C 63.12, H 4.71, N 2.34, S 2.67; found C 63.32, H 4.77, N 2.44, S 2.66.

**5b:** Pink solid. Recrystallized from $CH_2Cl_2$/*n*-hexane; yield 0.20 g, 66%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.5–2.7 (m, 8 H, 2× $PCH_2CH_2P$), 3.6 (m, 1 H, $OCH_3$), 4.2 (s, 1 H, N=C*H*), 6.9–7.2 (m, 26 H, 24-*H* of phenyl and 2-*H* of thienyl), 7.4–7.6 (m, 20 H, 16-*H* of phenyl and 4-*H* of aryl) ppm. $^{31}P\{^1H\}$NMR (121.7 MHz, $CDCl_3$): $\delta$ = –100.2 (s, MoP) ppm. IR (KBr): $\tilde{\nu}$ = 1558 (N=C) cm$^{-1}$. HRMS (NBA): *m*/*z* = 1127.2300 [M]$^+$; calcd. for $C_{64}H_{58}FMoN_2OP_4S$ 1127.2304. $C_{64}H_{58}BF_5MoN_2OP_4S$ (1212.88): calcd. C 60.38, H 4.82, N 2.31, S 2.64; found C 60.66, H 4.72, N 2.47, S 2.53.

**6:** Orange solid. Recrystallized from $CH_2Cl_2$/*n*-hexane; yield 0.14 g, 48%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.4–2.7 (m, 8 H, 2× $PCH_2CH_2P$), 4.2 (s, 1 H, N=C*H*), 7.1–7.4 (m, 28 H, 24-*H* of phenyl and 4-*H* of aryl), 7.5–7.8 (m, 19 H, 16-*H* of phenyl and 3-*H* of thienyl) ppm. $^{31}P\{^1H\}$NMR (121.7 MHz, $CDCl_3$): $\delta$ = –98.7 (s, MoP) ppm. IR (KBr): $\tilde{\nu}$ = 1574 (N=C) cm$^{-1}$. HRMS (NBA): *m*/*z* = 1113.2145 [M]$^+$; calcd. for $C_{63}H_{56}FMoN_2P_4S$ 1113.2147. $C_{63}H_{56}BF_5MoN_2P_4S$ (1198.85): calcd. C 63.12, H 4.71, N 2.34, S 2.67; found C 62.88, H 4.62, N 2.45, S 2.80.

**Electrochemical Studies:** The electrochemical experiments were performed on 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$^{-3}$ and 0.2 mol dm$^{-3}$ [$NBu_4$]$^+$[$BF_4$]$^-$ 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 H-type cell with a vitreous carbon working electrode as described previously.[53,54]

**Nonlinear Optical Measurements:** Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability $\beta$ of the molecules studied. The experimental set-up for hyper-Rayleigh measurements is similar to that presented by Clays and Persoons.[55] The incident laser beam came from a Q-switched Nd:YAG laser operating at a 10 Hz repetition rate with approximately 10 mJ of energy per pulse and a pulse duration (FWHM) of roughly 12 ns at the fundamental wavelength of 1064 nm. The incident power could be varied using a combination of a half wave-plate and Glan polarizer. The incident beam was weakly focused (beam diameter ca. 0.5 mm) into the solution contained in a 5-cm cuvette. The hyper- Rayleigh signal was collimated using a high numerical aperture lens passed through an interference filter with a full width at half maximum transmission of 3.3 nm centred on the second harmonic wavelength (532 nm) before being detected by a photomultiplier (Hamamatsu model H9305–04). The current pulse from the photomultiplier was integrated using a Stanford Research Systems gated box-car integrator (model SR250) with a 20 ns gate width. The hyper-Rayleigh signal was normalized at each pulse using the second harmonic signal from a 1 mm quartz plate to compensate for fluctuations in the temporal profile of the laser pulses due to longitudinal mode beating. Chloroform was used as a solvent, and the $\beta$ values were calibrated using a reference solution of *p*-nitroaniline [*p*NA also dissolved in chloroform at a concentration of $10^{-2}$ M (external reference method)].[15,49] The concentrations of the solutions under study were chosen so that the corresponding hyper-Rayleigh signals fell well within the dynamic range of both the photomultiplier and the box-car integrator. All solutions were filtered (0.2 μm porosity) to avoid spurious signals from suspended impurities. The small hyper Rayleigh signal that arises from a neat solution of chloroform was measured separately and taken into account when calculating the values for the first hyperpolarizability. We estimate that the experimental uncertainties are approximately ±10% of the values quoted in Table 4. All the hyperpolarizability values are corrected for any detected fluorescence contribution.

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