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# Synthesis and NLO Properties of 4-(4*H*-Chalcogenopyran-4-ylidene and 4*H*-chalcogenochromen-4-ylidene)-1-(phenylthio)but-2-enylidene Complexes – Electronic Influence of the Carbene Fragment

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The synthesis of 4-(4*H*-chalcogenopyran-4-ylidene and 4*H*-chalcogenochromen-4-ylidene)-1-(phenylthio)but-2-enylidene complexes is described and their non-linear optical (NLO) properties have been investigated (as $\mu\beta$ by EFISH). NMR studies and X-ray crystallographic analyses show that the (phenylthio)carbene fragment has a better electron-withdrawing capability than the methoxy analogues and, likewise, the corresponding thiocarbenes have a more significant pyrylium character. The $\mu\beta$ values of these complexes were obtained from EFISH experiments. The microscopic NLO response is sensitive to the nature of the intracyclic chalcogen atom, the nature of the metal centre and the benzo-annulation of the heterocycle.

## Introduction

Due to the strong electron-withdrawing effect of the (carbene)pentacarbonylmetal fragment, alkenyl Fischer carbene complexes have been exploited extensively for synthetic purposes. The utility of these unsaturated organometallic reagents in the Dötz reaction[1] in 1,2-, 1,4- and 1,6-addition reactions[2] or in the synthesis of heterocyclic compounds by means of various cycloaddition processes[3] is well documented. In the field of organometallic complex utilisation for NLO applications,[4] this electronic ability has made the pentacarbonyl(methoxy- or aminocarbene)metal fragments attractive candidates as acceptors in push-pull structures.[5] Association by means of a π-spacer to classic organic or organometallic donors such as *para*-(dimethylamino)benzyl[6] or ferrocenyl[7] groups has proved the efficiency of this method. High values of the first molecular hyperpolarisability $\beta$ have been determined by Hyper Raleigh Scattering (HRS). The influences of the metal (W or Cr),[5] the unsaturated chain length[6,7] and the solvent[7] on the $\beta$ values have been investigated. The results have been analysed in the context of the two-level model developed by Oudar and Chemla[8] which is based on the predominance of a single electronic transition despite the presence of more than one electronic transition in the visible region.[7]

In fact, the role of the organometallic carbene fragment is not well understood. For aminocarbene complexes, polarisation of the π-cloud by the electronic inductive effect of the $M(CO)_5$ moiety is responsible for the important NLO response.[6] The influence of an MLCT transition is minimised due to the lack of conjugation between the unsaturated chain and the carbene fragment.[9] On the other hand, noticeable $\beta$ values were also obtained for highly π-conjugated unsaturated methoxycarbene complexes.[5] It is worth noting that despite significant electronic differences between these two classes of carbenes, a systematic comparison between them has never been carried out. In addition, surprisingly, there are no reports on the NLO properties of unsaturated (alkylthio)- or (phenylthio)carbene complexes.

In fact, unlike their alkoxy or amino counterparts, (alkenyl)(thio)carbene complexes are rare compounds.[10] Their properties and reactivity require further elucidation.[11] Only some unsaturated (alkylthio)- and (phenylthio)carbenes have been reported by Aumann et al. using a condensation reaction between non-enolizable aldehydes (benzaldehyde, cinnamaldehyde) and the carbanion of $CH_3(SR)$-

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C=M(CO)$_5$ (M = Cr, W).[10] The low p$K_a$ values which characterise these complexes[12] [p$K_a$ = 8.37 for CH$_3$-(SCH$_3$)C=W(CO)$_5$ compared with 12.36 for CH$_3$(OCH$_3$)-C =W(CO)$_5$] enabled deprotonation by NEt$_3$. On the other hand, we have previously shown that 4*H*-pyran-4-ylidene fragments act as efficient electron-donors in push-pull methoxy Fischer-type carbene complexes.

The pyrylium character of these molecules was evaluated by using NMR spectroscopy, X-ray crystallographic measurements, DFT calculations and from their reactivity towards nucleophilic reagents.[2b,13] More recently, we have reported the NLO properties (as $\mu\beta$ by EFISH) of (4*H*-chalcogenopyran-4-ylidene and 4*H*-chalcogenochromen-4-ylidene)-1-methoxyalkenylidene complexes.[14] The $\mu\beta$ product is sensitive to the length of the unsaturated spacer, the nature of the chalcogen atom and to benzo-annulation of the heterocycle. Herein, we wish to report the formation and, for the first time, the first hyperpolarisability measurements of (phenylthio)carbene complexes. In addition, from NMR spectroscopic studies and X-ray structure analyses, we have shown that the carbonyl[(phenylthio)carbene]metal fragment acts as a powerful electron-withdrawing group. Comparison with analogous methoxycarbenes has been carried out.

## Results and Discussion

### Synthesis

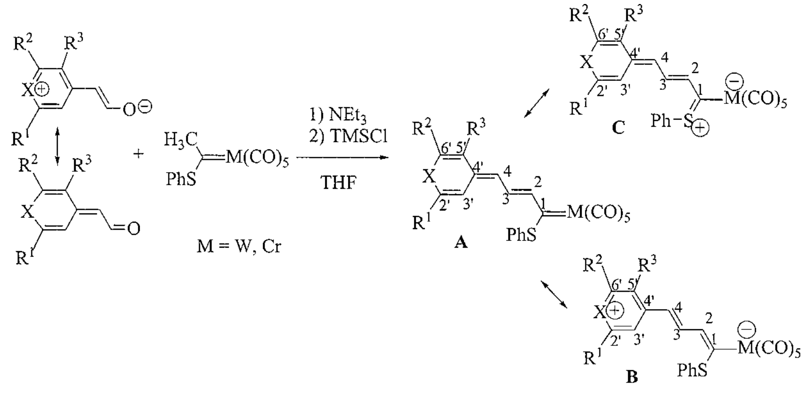
To obtain the expected donor-acceptor structures, we first chose to repeat Aumann's procedure[10] using the appropriate heterocyclic aldehydes **1a**–**1e**[15] and the carbanion produced from CH$_3$(PhS)C=W(CO)$_5$ by treatment with NEt$_3$, but this was unsuccessful. Addition of chlorotrimethylsilane (TMSCl) to the reaction mixture induced an instant colour change from red-orange to blue. After hydrolysis and purification by silica-gel chromatography, the intense dark blue condensation products **2a**–**2e** could be isolated. The moderate to low yields reported (Scheme 1) are the consequence of a decomplexation reaction which arises during the workup leading to the corresponding thioester.[16] The lack of reactivity without the assistance of TMSCl could be due to the high zwitterionic character of the heterocyclic aldehydes which prevents the carbanion addition on the carbon atom of the carbonyl function (Scheme 1).

We suggest that addition of the chlorosilane reagent produces alkenylpyrylium salts and favours the conjugated addition of the carbanion as the first step in this reaction. Such a zwitterionic form is insignificant in benzaldehyde and cinnamaldehyde and the condensation reaction does not require the use of TMSCl.[10,17]

The new heterocyclic carbene complexes **2a**–**2e** were characterised by $^1$H and $^{13}$C NMR spectroscopy, UV/Vis spectroscopy, FTIR spectroscopy, elemental analysis and high resolution mass spectrometry (for **2a**). All the data are consistent with the proposed structures. In particular, the $^3J_{H,H}$ coupling constant values (ca. 13 Hz) are in agreement with an (*E*) configuration for the C2–C3 double bond of the unsaturated chain (Scheme 1).

### NMR Studies – Evaluation of the Pyrylium Character of the Heterocyclic Complexes 2 in Solution

To obtain information about the pyrylium character of complexes **2** in solution, three NMR spectroscopic criteria were taken into account: (i) the chemical shift values of the 2-H and 3-H signals, (ii) the differences in $^3J_{H,H}$ values ($\Delta J$) across adjacent C=C and C–C bonds of the unsaturated chain and (iii) the $^{13}$C NMR chemical shift of the carbene carbon signal. First, with regards to the $^1$H NMR spectra of all compounds **2**, the chemical shift values of 2-H and 3-H display an oscillatory behaviour [$\delta$(3-H) > $\delta$(2-H) > $\delta$(4-H)] (Scheme 1). In particular the respective 3-H, 2-H signal position, which leads to positive $\Delta$ values [$\delta$(3-H) – $\delta$(2-H)]



**1a** R$^1$ = Ph, R$^2$= Ph, R$^3$ = H, X = O
**1b** R$^1$ = Ph, R$^2$ = Ph, R$^3$ = H, X = S
**1c** R$^1$ = Ph, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = O
**1d** R$^1$ = *t*Bu, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = O
**1e** R$^1$ = Ph, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = S

**2a** (40%) R$^1$ = Ph, R$^2$ = Ph, R$^3$ = H, X = O, M = W
**2b** (60%) R$^1$ = Ph, R$^2$ = Ph, R$^3$ = H, X = S, M = W
**2c** (17%) R$^1$ = Ph, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = O, M = W
**2'c** (20%) R$^1$ = Ph, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = O, M = Cr
**2d** (37%) R$^1$ = *t*Bu, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = O, M = W
**2e** (34%) R$^1$ = Ph, R$^2$ = R$^3$ = –CH=CH–CH=CH–, X = S, M = W

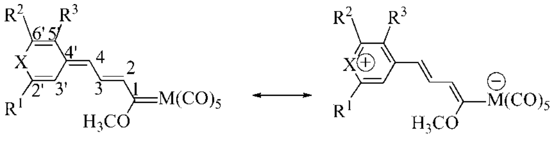
Scheme 1. Preparation of push-pull (phenylthio)carbene complexes **2**.

Table 1. NMR spectroscopic data for complexes **2**–**3**.[a]

| | **2a**[b] | **2b**[b] | **2c**[b] | **2d**[b] | **2e**[b] | **2′c**[b][14] | **3a**[c][14] | **3b**[c][14] | **3c**[c][14] | **3d**[c][15c] | **3e**[c][14] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta$ [$\delta$(3-H) – $\delta$(2-H)] [ppm] | 1.44 | 1.44 | 1.33 | 1.29 | 1.28 | 1.12 | 0.94 | 0.79 | 0.59 | 0.79 | 0.45 |
| $\Delta J$[d] [Hz] | –0.6 | –0.6 | 0.2 | 0.1 | 0.2 | 0.6 | 0.4 | 0.7 | 1.8 | 1.5 | 0.6 |
| $\delta^{13}$C [ppm] | 261.6 | 263.5 | 273.1 | 272.1 | 274.3 | 301.7 | 289.0 | 292.9 | 296.5 | 295.8 | 297.9 |

[a] NMR spectra were recorded in [D$_8$]THF solution. [b] Scheme 1. [c] Figure 1. [d] $\Delta J$ values: difference in $^3J_{\mathrm{H,H}}$ values across adjacent C(2)=C(3) and C(3)–C(4) bonds for compounds **2**–**3**.

(Table 1), suggests a highly conjugated push-pull structure for which the zwitterionic resonance form **B** is of importance in the valence bond description of the heterocyclic molecules (Scheme 1). As shown in Table 1, a similar trend has been observed for the methoxycarbene **3**,[14,18] analogously to **2** (Figure 1).



**3a** R$^1$ = Ph, R$^2$ = Ph, R$^3$ = H, X = O, M = W
**3b** R$^1$ = Ph, R$^2$ = Ph, R$^3$ = H, X = S, M = W
**3c** R$^1$ = Ph, R$^2$ = R$^3$= –CH=CH–CH=CH–, X = O, M = W
**3d** R$^1$ = *t*Bu, R$^2$ = R$^3$= –CH=CH–CH=CH–, X = O, M = Cr
**3e** R$^1$ = Ph, R$^2$ = R$^3$= –CH=CH–CH=CH–, X = S, M = W

Figure 1. Molecular structure of methoxycarbene complexes **3**.

As noted previously,[13a] this result differs from that found for other push-pull methoxy- and aminocarbene containing ferrocenyl,[7] *para*-(dimethylamino)phenyl[19] or 3,4-(methylenedioxy)phenyl groups[6] for which 2-H is more deshielded than 3-H (Table 2, Figure 2). For aminocarbenes, the predominance in solution of a conformation in which the (carbene)carbonylmetal fragment is perpendicular to the unsaturated part of the molecule would be responsible for this feature.[6,9] Owing to the low π-overlap, the inductive effect of the (carbene)carbonylmetal fragment controls the $^1$H NMR chemical shift values of the unsaturated chain and $\delta$(2-H) > $\delta$(3-H).

Table 2. $^1$H NMR spectroscopic data for push-pull alkenylidene complexes (Figure 2).

| R | Y | M | $\Delta$ [$\delta$(3-H) – $\delta$(2-H)] [ppm] | $\Delta J_{\mathrm{av.}}$ [Hz][a] | Solvent |
|---|---|---|---|---|---|
| Fc[7] | OMe | W | –0.22[b] | 3.8[b] | CDCl$_3$ |
| $p$-N(CH$_3$)$_2$C$_6$H$_4$[19] | OMe | W | –0.11[b] | 3.9[b] | CD$_2$Cl$_2$ |
| 3,4-CH$_2$O$_2$C$_6$H$_4$[6] | N(CH$_2$)$_4$ | Cr | –0.10[b] | – | CDCl$_3$ |

[a] $\Delta J_{\mathrm{av.}}$ values: average difference in $^3J_{\mathrm{H,H}}$ values across adjacent C=C and C–C bonds. [b] Evaluated from NMR values found in refs.[6,7,19]

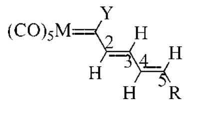


Figure 2. Structure of alkenyl Fischer-type carbene complexes.

It can be noted that the Δ values [$\delta$(3-H) – $\delta$(2-H)] of the (phenylthio)carbenes **2** are larger than those of methoxycarbenes **3**, indicating that the contribution of the pyrylium resonance structure in **3** is of lesser importance than in **2**. However, the $^1$H NMR chemical shift differences should reflect other factors such as the anisotropic effect of the phenyl group linked to the sulfur atom. Therefore, a comparison between the electronic influence of the methoxy- and the (phenylthio)carbene group requires other criteria.

Previously, it has been emphasised that the variation of $^3J_{\mathrm{H,H}}$ values along a conjugated polyene chain provides a good estimate of the C–C bond lengths (or bond orders).[20] In push-pull molecules containing a similar donor (acceptor), the so-called bond length alternation (BLA) depends on the strength of the acceptor (donor). As a consequence, the difference $\Delta J$ between the coupling constant $^3J_{\mathrm{H,H}}$ of concomitant C–C bonds ranges from 6.5 Hz for unconjugated molecules to 0 Hz for molecules in which all the C–C bond lengths are equal (cyanine limit). As shown in Table 1, calculated $\Delta J$ values for carbenes **2** and **3** are slightly negative or positive, in accordance with a reduced bond length alternation and, therefore, indicating a large degree of intramolecular charge transfer. Two features are noteworthy:

(1) The phenylthio complexes display lower $\Delta J$ values than those of their methoxy counterparts, in agreement with the better electron-withdrawing ability of the thiocarbene group as found above from the Δ [$\delta$(3-H) – $\delta$(2-H)] criterion. The negative values found for **2a** and **2b** strongly suggest that these molecules approach or even surpass the cyanine limit (predominance of resonance structure **B**) (Scheme 1). As proposed by Ali and Bernasconi from p$K_a$ values and kinetic constant determinations for both classes of complexes, the electronic difference can be mainly attributed to the smaller π-donor effect of the SR group compared with that of the methoxy group.[12] As a consequence, in complexes of type **2**, the conjugation between the ends of the molecule through the unsaturated chain is increased. However, concerning the π-effect strength of the SR group in Fischer-type carbene complexes, it should be noted that opposite conclusions were drawn from X-ray crystallographic data[21] and dynamic NMR studies (Figure 3).[22] In this context, the $^{13}$C NMR chemical shift values of the carbene carbon atom are of interest. In Fischer-type carbenes, the large upfield shift of the carbene carbon signal, when the heteroatom substituent is changed from an alkoxy to an amino group, has been attributed to the greater ability of the nitrogen atom to participate in dative π-bonding with the carbene carbon atom.[23] As shown in Table 3, such a

difference exists in (4*H*-pyran-4-ylidene)alkenylidene complexes (comparison between the carbene carbon chemical shifts of complexes **4** and **3a**). Accordingly, the intramolecular charge transfer in donor-acceptor unsaturated amino complexes[13] is limited due to the predominance of a resonance form involving the lone pair of the nitrogen atom of the amino group and the p-orbital of the carbene carbon atom. The chemical shift difference $\Delta$ [$\delta$(3-H) – $\delta$(2-H)] and the $\Delta J$ value found for the unsaturated aminocarbene complex **4** also support this electronic description. Since the PhS group in complex **2** seems to possess a lesser $\pi$-electron-donating capability compared with that of a methoxy group, the upfield shift observed for the carbene carbon signal of **2a** (Table 3) seems, at first glance, to be surprising. This finding, which is in sharp contrast to the usually observed chemical shift [$\delta(C_{carb,thio}) > \delta(C_{carb,methoxy})$],[24] should again reflect the donor-acceptor intramolecular charge transfer enhancement for the thiocarbene complexes. It is actually well established that along a series, the $^{13}C$ NMR carbene carbon chemical shift is sensitive to the electronic influence of the ligand.[13b]

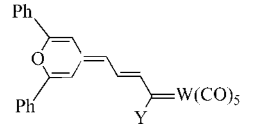


Figure 3. Structure of (4*H*-pyran-4-ylidene)alkenylidene complexes.

Table 3. NMR spectroscopic data for selected push-pull (4*H*-pyran-4-ylidene)alkenylidene complexes (Figure 3).

| | Y | $\Delta$ [$\delta$(3-H) – $\delta$(2-H)] [ppm] | $\Delta J$ [Hz] | $^{\delta 13}C$ [ppm] |
|---|---|---|---|---|
| **3a** | OMe | 0.94 | 0.4 | 289 |
| **4**[13a] | $N(CH_2)_4$ | –0.03 | 3.8 | 244 |
| **2a** | SPh | 1.44 | –0.6 | 261 |

(2) For the same organometallic phenylthio or methoxy fragment, $\Delta J$ values appear to increase from the pyran to the benzopyran series (methoxy and thiocarbene) (Table 1). This trend, which does, however, have an exception (see NMR values of **3e**), suggests a decrease in the electron-donor strength upon benzo-annulation (Table 1). Accordingly, the pyrylium characters of molecules **2a**, **2b**, **3a** and **3b** are greater than those of **2c**, **2d**, **3c** and **3d**, respectively. This view is corroborated by the low-field chemical shift values of the carbene carbon signals observed (even for **3e**) for the fused ring compounds. It should be noted that the chemical shift difference $\delta(C_{carb,benzopyran}) - \delta(C_{carb,pyran})$ is more pronounced for the (phenylthio)carbene indicating the great sensitivity of these complexes to $\pi$-electronic effects.

Very recently, effects of successive benzo-fusions for pyridinium acceptors in push-pull zwitterionic chromophores have been reported.[25] In such cases, and in agreement with the present results, it has been found that the annulation favours the neutral form thanks to the aromatic character of the fused benzene ring.

Finally, it is worth noting that the $\Delta J$ values reported here and those found for analogous derivatives of **3** of increasing length[14,15] are much smaller than those calculated from previous studies for unsaturated methoxy complexes containing ferrocenyl[7] or *para*-(dimethylamino)phenyl donor groups[19] ($\Delta J_{av.} > 3.5$ Hz) (Table 2, Figure 2). This once again confirms the great electron-donor capability of the proaromatic pyran and benzopyran heterocycles and the powerful electron-withdrawing ability of the carbonyl-[(phenylthio)carbene]metal group.

### X-ray Analysis of 2a

Blue single crystals of **2a** suitable for the X-ray analysis were obtained by slow concentration of a diethyl ether/petroleum ether solution. The molecular view with the atom labelling is shown in Figure 4. As indicated by the ORTEP drawing, the determination of the (*E*) stereochemistry based on the *J* coupling constant values is correct. The molecule exhibits a nearly planar conformation. However, the phenyl ring linked to the sulfur atom is in a *syn* conformation and is twisted by 88.8(5)° with respect to the plane of the conjugated chain. In addition, C(3) and C(4) lie slightly away from the ideal plane. The –CH=CH–C(SPh)=W(CO)$_5$ fragment is in an *syn* conformation.

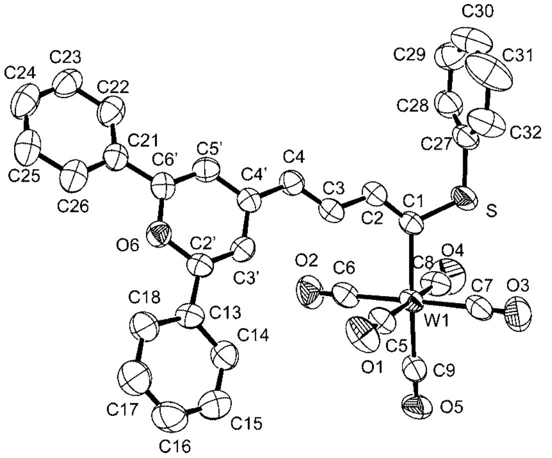


Figure 4. ORTEP drawing of **2a** showing the atom numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: W(1)–C(1) 2.251(7), S–C(1) 1.719(7), C(1)–C(2) 1.398(10), C(2)–C(3) 1.377(9), C(3)–C(4) 1.373(9), C(4)–C(4′) 1.389(9), O(6)–C(6′) 1.359(8), O(6)–C(2′) 1.370(8), C(2′)–C(3′) 1.336(10), C(3′)–C(4′) 1.429(10), C(6′)–C(5′) 1.350(10), C(5′)–C(4′) 1.435(9).

Assuming that the solid-state molecular structure reflects the conformation of **2a** in solution, this situation should have an influence on the NLO properties (see below). In accordance with the NMR investigations, the nearly equal C(2)–C(3), C(3)–C(4) bond lengths together with the large C(1)–W bond length [2.251(7) Å] are indicative of significant delocalisation between the heterocyclic oxygen atom and the metal centre through the unsaturated backbone (large pyrylium character). On the pyran side, the intracyclic C–C and C–O bond length values appear to be close to those found for other (4*H*-pyran-4-ylidene)alkenylidene complexes for which DFT calculations and X-ray analyses have indicated a pyrylium character.[13] It is noticeable that the 2,6-diphenylpyrylium salts bearing a 4-(dimethylamino)benzyl group donor display similar intraheterocyclic C–O and C–C bond lengths due to pronounced 4*H*-pyran-4-ylidene character.[26] Again, in accordance with the significant contribution from the pyrylium form, the exocyclic C=C bond length (1.389 Å) has single-bond character. This value is greater than that determined for lesser conjugated bis(4*H*-pyrans) (1.375 Å)[27] and is close to those reported by us for other methoxy(4*H*-pyran-4-ylidene)alkenylidene complexes.[2b,13b] Moreover, it is worth remarking that in chromenylideneacetaldehyde hydrazone containing $[(\eta^6\text{-arene})CpFe]^+$ as an electron-accepting group, the exocyclic C=C bond is 1.354 Å long indicating a weak benzopyrylium form.[28] Finally, the C–SPh distance (1.719 Å), which lies within the normal range (C–S, C=S),[20] provides evidence for back-bonding donation from the heteroatom lone pair and the carbene carbon atom (resonance structure **C**) (Scheme 1). It is noticeable that a lower value was reported from the pentacarbonyl[methyl(phenylthio)carbene]chromium complex X-ray analysis.[20b]

### Linear and Non-Linear Optical Properties

The UV/Vis electronic spectra of molecules **2** were recorded in four solvents of varying polarity (Table 4). For **2a**, **2b**, **2c** and **2′c**, a rapid decomplexation reaction occurs in DMSO ($\varepsilon_{25\,^\circ\mathrm{C}} = 48.9$) leading to the corresponding thioester.[10] In such cases $CH_3CN$ ($\varepsilon_{25\,^\circ\mathrm{C}} = 37.5$) was used. The UV/Vis spectra of the (phenylthio)carbenes **2** consist of two intense absorption bands in the visible region (Table 4). By comparison with the spectra of analogous methoxycarbene complexes, for which DFT computations have been performed,[13b] the lower and the higher energy bands can be assigned to the metal-to-ligand charge transfer transition (MLCT), corresponding to the HOMO–LUMO transition, and the intraligand charge transfer transition (ILCT or π→π*), respectively. In these complexes, the HOMO and the LUMO electronic density is mainly located on the metal centre and on the ligand, respectively.[13] However, despite the great similarity of the spectra, it can be noted that compared with their methoxy counterparts **3**, the corresponding electronic transitions of **2** are red-shifted, possibly as a consequence of a lowering of the π*-level (LUMO). On the other hand, under the intracyclic O→S atom substitution, a bathochromic shift can be observed for the two bands. Such a trend, also found for the methoxycarbenes,[14] should be a consequence of a decrease in the HOMO–LUMO and π→LUMO gaps. MNDO calculations have shown that such HOMO–LUMO gap lowering upon O→S substitution exists in push-pull chalcogenopyrylium salts.[29] Substitution of the Cr atom for W (**2c**, **2′c** comparison) leads to a clear bathochromic shift.

As expected, the MLCT band appears to be more sensitive to the metal change. The presence of a *t*Bu electron-donating group in **2d** (which, unlike a phenyl substituent, is not capable of conjugative interaction with the chalcogenobenzopyran ring) increases the energy of both transitions. Finally, influence of the benzo-annulation on the maximum absorptions seems more complex and depends on the nature of the chalcogen atom (Table 4) and on the solvent polarity. Thus, for **2a** and **2b**, the two characteristic CT bands exhibit a hypsochromic shift when the solvent polarity is increased, as expected from the zwitterionic character of the ground state (see above). It is worth remarking that for the less zwitterionic methoxy complexes **3a** and **3b** (Figure 1), analogous to **2a** and **2b**, a bathochromic shift occurs for the MLCT transition.[14] For the chalcogenobenzopyran complexes **2c**, **2d** and **2e**, a weak solvent influence can be observed for both electronic transitions, and an inversion of the solvatochromism cannot be totally excluded. The behaviour of the carbenechromium complex **2′c** differs from that of **2c** since the solvent change has a small influence on the π→π* transition and the MLCT transition is only sensitive to the less polar solvents utilised ($CCl_4$, $CH_2Cl_2$ and $CH_3COCH_3$) (observation of a hypsochromic shift). In conclusion, the presence of two intense electronic transitions in the visible region should make the interpretation of the NLO results more difficult and precludes relevant analysis based on the two-level model.[8]

Second-order nonlinear properties were studied in $CHCl_3$ solution ($\varepsilon_{25\,^\circ\mathrm{C}} = 4.7$) at 1907 nm by the electric-field-induced second-harmonic generation technique (EFISH) which provides information about the scalar product $\mu\beta$ $(2\omega)$ of the vector component of the first hyperpolarisability tensor $\beta$ and the dipole moment vector. This product

Table 4. UV/Vis absorption properties of compounds **2** in various solvents.

| | Solvent | $\lambda_{max}$ [nm] ($\varepsilon \times 10^{-4}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | **2a** | **2b** | **2c** | **2d** | **2e** | **2′c** |
| $\lambda_1$ ($\varepsilon$) | $CCl_4$ | 538 (4.8) | 565 (3.2) | 541 (2.9) | 526 (3.7) | 563 (3.3) | 549 (3.5) |
| $\lambda_1$ ($\varepsilon$) | $CH_2Cl_2$ | 532 (4.1) | 561 (3.2) | 540 (3.4) | 524 (3.4) | 567 (2.3) | 549 (3.7) |
| $\lambda_1$ ($\varepsilon$) | $(CH_3)_2CO$ | 521 (4.2) | 551 (2.5) | 536 (1.1) | 519 (3.0) | 562 (2.3) | 544 (3.8) |
| $\lambda_1$ ($\varepsilon$) | $CH_3CN$ | 518 (3.1) | 547 (2.0) | 534 (2.2) | 518 (2.5) | 561 (1.4) | 544 (3.0) |
| $\lambda_1$ ($\varepsilon$) | DMSO | [a] | [a] | 538 (1.9) | 522 (2.5) | [a] | [a] |
| $\lambda_2$ ($\varepsilon$) | $CCl_4$ | 673 (3.4) | 695 (2.5) | 663 (1.7) | 649 (2.0) | 679 (2.2) | 690 (1.3) |
| $\lambda_2$ ($\varepsilon$) | $CH_2Cl_2$ | 658 (5.4) | 693 (4.3) | 657 (3.0) | 638 (3.1) | 682 (2.3) | 670 (1.8) |
| $\lambda_2$ ($\varepsilon$) | $(CH_3)_2CO$ | 652 (8.1) | 689 (5.0) | 652 (1.3) | 631 (3.5) | 681 (2.9) | 662 (2.3) |
| $\lambda_2$ ($\varepsilon$) | $CH_3CN$ | 648 (6.4) | 687 (4.4) | 654 (2.6) | 630 (3.2) | 682 (1.9) | 663 (1.9) |
| $\lambda_2$ ($\varepsilon$) | DMSO | [a] | [a] | 663 (3.1) | 636 (4.0) | [a] | [a] |

[a] In DMSO, decomplexation reactions occur.

Table 5. $\mu\beta$ values for **2**–**3**.

| | **2a** | **2b** | **2c** | **2d** | **2e** | **2′c** | **3a**[14] | **3b**[14] | **3c**[14] | **3d**[15c] | **3e**[14] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\mu\beta$ [$10^{-48}$ esu][a] | 173 | 518 | 420 | 374 | 421 | 140 | 505 | 665 | 219 | 310 | 402 |

[a] $\mu\beta(2\omega)$ at 1907 nm in $CHCl_3$. Molecular concentrations used for the measurements were in the range $10^{-3}$ to $10^{-2}$ M; 3-methyl-4-nitroaniline (MNA) for which $\mu\beta(CHCl_3) = 71.06\times10^{-48}$ esu was used as an external reference. $\mu\beta\pm20\%$.

is derived according to Equation (1) and, considering $\gamma_0(-2\omega,\omega,\omega,0)$, the third-order term is negligible for the push-pull compounds under study. This approximation is usually used for push-pull organic and organometallic molecules.

$$\gamma_{EFISH} = \mu\beta/5kT + \gamma_0(-2\omega,\omega,\omega,0) \qquad (1)$$

All complexes were thus tested away from resonance. It should be noted that the sign and values of $\mu\beta$ depend on the "direction" of the transition implied in the NLO phenomena and on the direction of the ground-state dipole moment. When $\beta$ and $\mu$ are parallel (antiparallel), positive (negative) maxima $\mu\beta$ values are reached.

DFT calculations performed on analogous methoxycarbenes have shown that the ground-state dipole moment is governed by the pyrylium character of these molecules (Figure 5).[13b] However, a slight variation in the dipole moment orientation can occur according to the degree of *syn* or *anti* conformation of the complexes (see X-ray analysis of **2a**).[30]

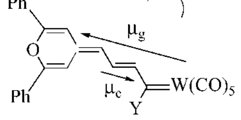


Figure 5. Orientations of the ground-state and excited-state (MLCT) dipole moment vectors.

As for the methoxycarbenes[14] **3**, all the $\mu\beta$ values of complexes **2** (Table 5) are large and positive, indicative of the implied transition(s) of the first excited states which are more polarized than the ground states and a vectorial $\beta$ with almost the same direction as the ground-state dipole moment. This is not in accordance with the negative solvatochromism or the low solvent polarity influence observed for the MLCT and π-π* transitions in **2a**–**2e** and **2′c**. Moreover, the MLCT charge transfer direction implies an excited dipole moment vector $\mu_e$ opposite to the ground-state dipole moment $\mu_g$ vector.[8] Therefore, this transition may only play a minor role in the first hyperpolarisability, since positive $\mu\beta$ values are found. On the other hand, the π→π* charge transfer implies a corresponding $\mu_e$ almost parallel to $\mu_g$. A positive or a negative $\mu\beta$ value could be expected with respect to the contribution of the two limit forms **A** and **B** (Scheme 1). Despite the complexity of this situation, important information can be deduced from the $\mu\beta$ values shown in Table 5.

First, substitution of W by Cr (**2c**, **2′c** comparison) lowers the first hyperpolarisability response. This shift, as previously[5] proposed, should be the consequence of a more polarisable metal electron shell for the W atom. However, a part of the $\mu\beta$ decrease should reflect the variation of the dipole moment (see NMR: $\Delta J$ values). From a comparison of **2a** and **2b** it seems once again (see **3a**, **3b**, **3c** and **3e** $\mu\beta$ values, Table 5)[14] that the presence of an intracyclic pyran sulfur atom favours the hyperpolarisability response. This effect could be relevant to the greater polarisability of the electrons of the sulfur compared with the electrons of the oxygen. However, it can be noted that this heteroatomic influence is not operative in the chalcogenobenzopyran structure, since similar responses are found for **2c** and **2e**. It seems that the presence of a fused benzene ring produces subtle electronic differences which make the analysis more difficult. On the other hand, annulation produces an increase in $\mu\beta$ for O-heterocycles and a decrease for S-heterocycles. This last result is in line with the behaviour of analogous methoxycarbenes (see **3a**, **3c** and **3b**, **3e** $\mu\beta$ values, Table 5).[14] It should be the consequence of the lower π-electron mobility in **2e** owing to the aromatic character of the appending benzene ring. The low $\mu\beta$ value observed for the pyran complex **2a**, which is responsible for the inverse $\mu\beta$ evolution for the two series, merits comments. As stated from NMR spectroscopic data, the pyrylium character of **2a** is important and is close to the thiopyrylium character of **2b** (see $\Delta J$ value, Table 1). Consequently, the greater aromaticity of the pyran ring in **2a**[29,31] should in part explain the lower NLO response. Finally, for the (phenylthio)carbenes, substitution of a phenyl group by a tertiary butyl group slightly reduced the $\mu\beta$ value (**2c**, **2d** comparison). The opposite trend (slight increase) may be observed for the methoxycarbenes (**3c**, **3d** comparison). In conclusion, from $\mu\beta$ and $\Delta J$ value comparison, it seems that the BLA factor has a minor influence on the NLO behaviour of these complexes.

## Conclusion

In the 4-(4*H*-chalcogenopyran-4-ylidene and 4*H*-chalcogenochromen-4-ylidene)-1-(phenylthio)but-2-enylidene complexes **2**, the carbonyl[(phenylthio)carbene]metal fragment acts as an exceptional electron-accepting group. Consequently, the pyrylium character is important and some of the complexes under investigation surpass the cyanine limit in [D$_8$]THF. From comparisons of NMR spectroscopic data, it seems that the carbonyl[(phenylthio)carbene]metal group in complexes **2** is a better electron-withdrawing group than a carbonyl(methoxycarbene)metal group. A single-crystal X-ray diffraction analysis of compound **2a** has shown an electronic structure which enables conjugation between the intracyclic oxygen atom and the metal centre which is in accordance with the pronounced pyrylium character of the heterocycle. The first hyperpolarisability of the thiocarbenes have been measured by the EFISH technique. The $\mu\beta$ values are close to those found for methoxycarbenes of similar lengths[14] and are sensitive to the intracyclic heteroatom, the benzo-annulation and the metal. However, the presence of two absorption bands in the visible region precludes analysis based only on a simple model. Theoretical calculations should be necessary to obtain more information on the electronic transitions and excited states implied by the NLO properties.

## Experimental Section

**General Remarks:** All preparations involving organometallic (4*H*-pyran-4-ylidene)alkenylidene compounds were carried out under dry nitrogen. Solvents were dried and distilled before use according to standard procedures.[32] $^1$H and $^{13}$C NMR spectra were recorded in [D$_8$]THF using a Bruker 500 MHz spectrometer. Infrared spectra were recorded with a Perkin–Elmer FTIR-1000 spectrometer using KBr plates. Microanalyses were performed using a Microanalyseur Flash EA 1112 instrument and mass spectra were obtained using a high-resolution MS/MS Zab spec Tof micromass system at the Centre Régional de Mesures Physiques de l'Ouest Université de Rennes 1. Optical absorption spectra were measured with a Perkin–Elmer Lambda 25 spectrophotometer.

**X-ray Structure Determination:** Blue single crystals of **2a** suitable for X-ray analysis were obtained by slow concentration of a diethyl ether/petroleum ether solution and were mounted on a Nonius four-circle diffractometer equipped with a CCD camera and a graphite-monochromated Mo-$K_\alpha$ radiation source ($\lambda$ = 0.71073 Å) at the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data collection was performed at 293(2) K. $C_{32}H_{20}O_6SW$, $M$ = 716.39, monoclinic, $P2_1/c$, $a$ = 9.0690(2), $b$ = 14.7950(2), $c$ = 21.4990(5) Å, $\beta$ = 100.432(1)°, $V$ = 2836.9(1) Å$^3$, $Z$ = 4, $\rho_{\text{calcd.}}$ = 1.677 g cm$^{-3}$. 12109 structure factors were collected before merging to yield 6506 unique intensities ($R_{\text{int}}$ = 0.0482). The structure was solved with SHELXS-97.[33] The refinement of 361 parameters against $F^2$ of 6506 unique intensities [4246 observed intensities $I > 2\sigma(I)$] was performed with SHELXL-97[34] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model in calculated positions. Final residuals: $R$ = 0.0548, $wR$ = 0.1247. CCDC-297214 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Synthetic Methodology: General Procedure for the Synthesis of Complexes 2a–2e:** A solution of the aldehydes[15] **1a**–**1e** ($1.1\times10^{-3}$ mol) with 1 equiv. of $CH_3(SPh)C{=}W(CO)_5$[10,35] ($1.1\times10^{-3}$mol), 3 equiv. of $(CH_3)_3SiCl$ (TMSCl) and 3 equiv. of $(C_2H_5)_3N$ in THF (20 mL) was stirred at room temperature. The reaction, monitored by TLC, showed that the starting carbene complex quickly disappeared. Degassed water was poured onto the blue reaction mixture and the product was extracted with diethyl ether. The extract was dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel plates (elution with petroleum ether/dichloromethane, 70:30). The condensation products **2a**–**2e** were isolated after evaporation of the solvent and recrystallised from diethyl ether/petroleum ether solutions.

**Synthesis of Analogous Complex 2′c:** The above procedure was applied, but using the (phenylthio)carbene complex $CH_3(SPh)$-$C{=}Cr(CO)_5$.

**Complex 2a:** Decomposition > 250 °C. MS (FAB): calcd. for $C_{29}H_{20}O_3SW$ [M – 3 CO]$^{+\cdot}$ 632.0643, found 632.0660. IR (KBr pellet): $\tilde{\nu}$ = 2049, 1928, 1893, 1641, 1519, 1502, 1482, 1342, 1245, 1156, 963, 934, 882, 792, 767, 680, 591 cm$^{-1}$. $^1$H NMR ([D$_8$]THF): $\delta$ = 8.39 (t, $^3J$ = 12.9 Hz, 1 H, 3-H), 7.99 (m, 4 H, Ph), 7.59 (m, 3 H, Ph), 7.58 (s, 1 H, 3-H), 7.54 (m,3 H, Ph), 7.48 (m, 5 H, Ph), 7.24 (d, $^4J$ = 1.5 Hz, 1 H, 5-H), 6.95 (d, $^3J$ = 12.6 Hz, 1 H, 2-H), 6.04 (d, $^3J$ = 13.2 Hz, 1 H, 4-H) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 261.6 (C-1), 205.8 (C, CO), 200.8 (C, CO), 160.4 (C-2′), 160.2 (C-6′), 157.3 (C-3), 152.3 (C-4′), 138.95 (C-2), 134.2 (C, Ph), 132.6 (C, Ph), 132.4 (C, Ph), 132.2 (C, Ph), 130.4 (C, Ph), 130.3 (C, Ph), 130.2 (C, Ph), 130.1 (C, Ph), 126.8 (C, Ph), 126.7 (C, Ph), 118.0 (C-4), 111.9 (C-5′), 105.1 (C-3′) ppm.

**Complex 2b:** M.p. 162 °C. IR (KBr pellet): $\tilde{\nu}$ = 2051, 1902, 1878, 1529, 1472, 1276, 1168, 805, 747 cm$^{-1}$. $C_{30}H_{20}S_2W$ (628): calcd. C 52.47, H 2.75, S 8.75; found C 52.78, H 3.05, S 8.66. $^1$H NMR ([D$_8$]THF): $\delta$ = 8.40 (t, $^3J$ = 12.9 Hz, 1 H, 3-H), 7.93 (s, 1 H, 3′-H), 7.74 (m, 4 H, Ph), 7.56 (m, 3 H, Ph), 7.52 (m, 3 H, Ph), 7.50 (s, 1 H, 5′-H), 7.47 (m, 5 H, Ph), 6.97 (d, $^3J$ = 12.6 Hz, 1 H, 2-H), 6.24 (d, $^3J$ = 12.6 Hz, 1 H, 4-H) ppm. $^{13}$C NMR ([D$_8$]THF ): $\delta$ = 263.5 (C-1), 206.0 (C, CO), 200.6 (C, CO), 155.8 (C-3), 152.1 (C-4′), 150.1 (C-2′), 149.2 (C-6′), 139.8 (C-2), 138.8 (C, Ph), 137.4 (C, Ph), 137.1 (C, Ph), 134.2 (C, Ph), 132.0 (C, Ph), 130.6 (C, Ph), 130.5 (C, Ph), 130.4 (C, Ph), 128.5 (C-5′), 127.5 (C, Ph), 127.3 (C, Ph), 121.0 (C-3′) ppm.

**Complex 2c:** Decomposition > 250 °C. IR (KBr pellet): $\tilde{\nu}$ = 2052, 1906, 1615, 1529, 1505, 1487, 1350, 1272, 1170, 1123, 1011, 907, 795, 764, 682 cm$^{-1}$. $C_{30}H_{18}O_6SW$ (690): calcd.C 52.19, H 2.63, S 4.64; found C 52.56, H 2.89, S 4.78. $^1$H NMR ([D$_8$]THF ): $\delta$ = 8.55 (t, $^3J$ = 12.8 Hz, 1 H, 3-H), 8.11 (d, $^3J$ = 8.2 Hz, 1 H, benzo), 8.01 (2 H, m, Ph-H), 7.67 (ddd, $^3J$ = 8.4 Hz, $^3J$ = 7.1 Hz, 1 H, benzo), 7.60 (1 H, s, 3′-H), 7.56 (m, 4 H, benzo, Ph), 7.52 (m, 3 H, Ph), 7.50 (2 H, m, Ph), 7.36 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 7.1 Hz, 1 H, benzo), 7.22 (d, $^3J$ = 12.9 Hz, 1 H, 2-H), 6.80 (d, $^3J$ = 12.7 Hz, 1 H, 4-H) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 273.1 (C-1), 206.0 (C, CO), 200.4 (C, CO), 157.6 (C-2′), 156.9 (C-3), 154.0 (C-6′), 147.0 (C-4′), 141.2 (C-2), 139.0 (C, Ph), 134.0 (C, benzo), 133.8 (C, Ph), 132.8 (C, Ph), 132.3 (C, Ph), 130.8 (C, Ph), 130.6 (C, Ph), 130.1 (C, Ph), 126.9 (C, benzo), 126.8 (C, Ph), 125.3 (C-5′), 119.3 (C, benzo), 115.3 (C-4), 102.7 (C-3′) ppm.

**Complex 2d:** M.p. 170 °C. IR (KBr pellet): $\tilde{\nu}$ = 2052, 1914, 1622, 1563, 1534, 1508, 1477, 1462, 1349, 1309, 1267, 1232, 1183, 1164, 1135, 1104, 1024, 960, 936, 882, 862, 836, 808, 761, 751 cm$^{-1}$. $C_{28}H_{22}O_6SW$ (670): calcd. C 50.17, H 3.31, S 4.78; found C 50.30, H 3.41, S 4.56. $^1$H NMR ([D$_8$]THF): $\delta$ = 8.56 (t, $^3J$ = 12.8 Hz, 1 H, 3-H), 8.07 (dd, $^3J$ = 8.3 Hz, $^4J$ = 1.3 Hz, 1 H, benzo), 7.63 (ddd, $^3J$ = 8.4 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.3 Hz, 1 H, benzo), 7.52 (m, 3 H, Ph), 7.48 (m, 2 H, Ph), 7.43 (dd, $^3J$ = 8.4 Hz, $^4J$ = 1.0 Hz, 1 H, benzo), 7.33 (ddd, $^3J$ = 8.3 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.0 Hz, 1 H, 6′-H), 7.17 (d, $^3J$ = 12.9 Hz, 1 H, 2-H), 7.01 (s, 1 H, 3′-H), 6.72 (d, $^3J$ = 12.8 Hz, 1 H, 4-H), 1.40 (s, 9 H, CH$_3$) ppm. $^{13}$C NMR ([D$_8$]-THF): $\delta$ = 272.1 (C-1), 205.7 (C, CO), 200.3 (C, CO), 170.4 (C-2′), 157.9 (C-3), 154.4 (C-6′), 148.1 (C-4′), 140.5 (C-2), 139.0 (C, Ph), 133.9 (C, benzo), 133.9 (C, Ph), 130.8 (C, Ph), 130.6 (C, Ph), 126.6 (C, benzo), 125.3 (C, benzo), 122.1 (C-5′), 119.1 (C, benzo), 114.1 (C-4), 110.9 (C-3′), 37.2 [C, C(CH$_3$)$_3$], 28.2 (C, CH$_3$) ppm.

**Complex 2e:** Decomposition > 250°. IR (KBr pellet): $\tilde{\nu}$ = 2050, 1902, 1526, 1500, 1485, 1258, 1163, 1085, 962, 823, 750, 689 cm$^{-1}$. $C_{30}H_{18}O_5S_2W$ (706): calcd. C 51.01, H 2.57, S 9.08; found C 51.64, H 2.67, S 9.87. $^1$H NMR ([D$_8$]THF): $\delta$ = 8.54 (t, $^3J$ = 12.7 Hz, 1 H, 3-H), 8.28 (d, $^3J$ = 8.4 Hz, 1 H, benzo), 8.03 (s, 1 H, 3-H), 7.78 (dd, $^3J$ = 5.5 Hz, $^4J$ = 2.8 Hz, 2 H, Ph), 7.71 (d, $^3J$ = 8.0 Hz, 1 H, benzo), 7.58 (m, 1 H, benzo), 7.55 (m, 6 H, Ph), 7.51 (m, 2 H, Ph), 7.49 (m, 1 H, benzo), 7.26 (d, $^3J$ = 12.9 Hz, 1 H, 2-H), 7.07 (d, $^3J$ = 12.7 Hz, 1 H, 4-H). $^{13}$C NMR ([D$_8$]THF): $\delta$ = 274.3 (C-1), 206.1 (C, CO), 200.1 (C, CO), 156.2 (C-3), 148.2 (C-4′), 146.1 (C-2′), 142.1 (C-2), 138.9 (C, Ph), 138.0 (C, Ph), 131.0 (C, Ph), 130.7 (C, Ph), 130.4 (C, Ph), 129.8 (C-5′), 129.6 (C, benzo), 128.4 (C, benzo), 127.5 (C, Ph), 121.1 (C-4), 119.3 (C-3′) ppm.

**Complex 2′c:** Decomposition > 250°. IR (KBr pellet): $\tilde{\nu}$ = 2041, 1907, 1625, 1512, 1488, 1463, 1350, 1322, 1273, 1154, 1123, 1112, 964, 909, 884, 814, 763, 688, 654 cm$^{-1}$. $C_{30}H_{18}O_6SCr$ (558): calcd. C 64.51, H 3.25, S 5.74, found C 64.47, H 3.52, S 6.14. $^1$H NMR ([D$_8$]THF): $\delta$ = 8.55 (t, $^3J$ = 12.8 Hz, 1 H, 3-H), 8.07 (dd, $^3J$ = 8.2 Hz, $^4J$ = 1.3 Hz, 1 H, 5-H), 7.59 (s, 1 H, 3-H), 7.56 (m, 3 H, Ph), 7.42 (m, 4 H, 8-H, Ph), 7.45 (m, 2 H, Ph), 7.42 (d, $^3J$ = 13.1 Hz, 1 H, 2-H), 7.35 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.0 Hz, 1 H, 6-H), 6.76 (d, $^3J$ = 12.6 Hz, 1 H, 4-H) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 301.7 (C-1′), 227.6 (C, CO), 219.7 (C, CO), 157.2 (C-2), 153.9 (C-9), 153.2 (C-3′), 146.2 (C-4), 140.2 (C-2′), 133.8 (C, Ph), 132.9 (C, Ph), 132.2 (C, Ph), 130.8 (C, Ph), 130.5 (C, Ph), 130.1 (C, Ph), 126.7 (C-6 + C, Ph), 125.3 (C-5), 122.1 (C-10), 119.2 (C-8), 115.3 (C-4′), 102.3 (C-3) ppm.

**NLO Measurements:** NLO measurements were carried out using the Electric Field Induced Second Harmonic (EFISH) technique.[36] The data were recorded using a nanosecond Nd:YAG pulsed (10 Hz) laser operating at 1064 nm, equipped with a hydrogen cell (1 m long, 40 bar) for Raman shifting. The 1907 nm beam was selected and used as the fundamental for EFISH. The compounds were dissolved in chloroform at various concentrations (typically in the range of $1\times10^{-3}$ to $9\times10^{-3}$ mol L$^{-1}$) and a specific cell mounted on a translation stage was used. The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high voltage pulse (5 kV) synchronized with the laser pulse. The SHG signal was selected through a suitable interference filter, detected by a photomultiplier, and recorded by an oscilloscope. Translation of the cell allowed us to obtain the typical Maker fringes. The NLO response was analysed according to an already published procedure. 2-Methyl-4-nitroaniline was used as a reference ($\mu\beta = 71\times10^{-48}$ esu at 1907 nm) to determine the $\mu\beta$ value of our compounds.

**Supporting Information** (see footnote on the first page of this article): Table S1 lists the UV/Vis absorption properties of complexes **3** in various solvents.

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