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Electronic and Structural Effects on the Nonlinear Optical Behavior in Push−Pull TTF/Tricarbonyl Chromiun Arene Complexes

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A novel D−π−A system in which tetrathiafulvalene (TTF) and π-extended TTFs as strong electron donors are covalently connected to a tricarbonyl (η^6-arene)chromium complex as the acceptor moiety through a systematically increased conjugated bridge of vinylene units (**12a**−**c**, **16a**−**c**) have been synthesized by Wittig−Horner olefination reaction. The electronic spectra as well as the electrochemical data reveal a different behavior of TTF derivatives (**12a**−**c**) and of exTTF derivatives (**16a**−**c**). Cyclic voltammetry shows the influence of the tricarbonylchromium arene on the oxidation potentials in compounds **12a**−**c**, and no remarkable effect is observed for exTTFs (**16a**−**c**). The nonlinear optical properties of **12a**−**c** and **16a**−**c** have been calculated by using the ab initio CPHF/6-31G*//B3P86/6-31G* model, and the time-dependent density functional theory (TD-DFT) method has been used for the calculation of the electronic transitions. The calculations reveal that an intraligand charge-transfer transition (ILCT) and the metal to ligand charge-transfer transition (MLCT) are responsible for the nonlinear response. In addition, the large angles formed by the ground-state dipole moment and the vectorial hyperpolarizability are responsible for the $\mu\beta$ values determined experimentally by the EFISH technique.

Introduction

During the past decade, great effort has been devoted to the synthesis of π-conjugated donor−acceptor (D−A) organic molecules in the search of new materials exhibiting nonlinear optical (NLO) properties. This synthetic effort has allowed the determination of the structural features required to obtain compounds with enhanced quadratic molecular response (hyperpolarizability β) and with a realistic application in the emerging field of "molecular electronics and photonics".[1] At the molecular level, donor−π-conjugated bridge−acceptor (D−π−A) structures showing a charge-transfer process from the D to the A moiety and, therefore, a significant difference between both ground-state and excited-state dipole moments, are the best candidates for attaining high hyperpolarizabilities.[1]

Among the different chemical compounds investigated for NLO purposes, transition metal organometallics, and coordination complexes are an important class with some remarkable β values.[2] In addition, metals can have a large diversity of oxidation states and ligand environments, and the presence of polarizable d electrons is responsible for the interesting NLO effects observed in these systems.[3] Recently, the NLO response of different metal complexes has been modulated (on and off) by means of reversible redox active moieties (octamethylferrocene, Ru(II) complexes) able to act as efficient switches.[4] In these systems, the value of β is decreased

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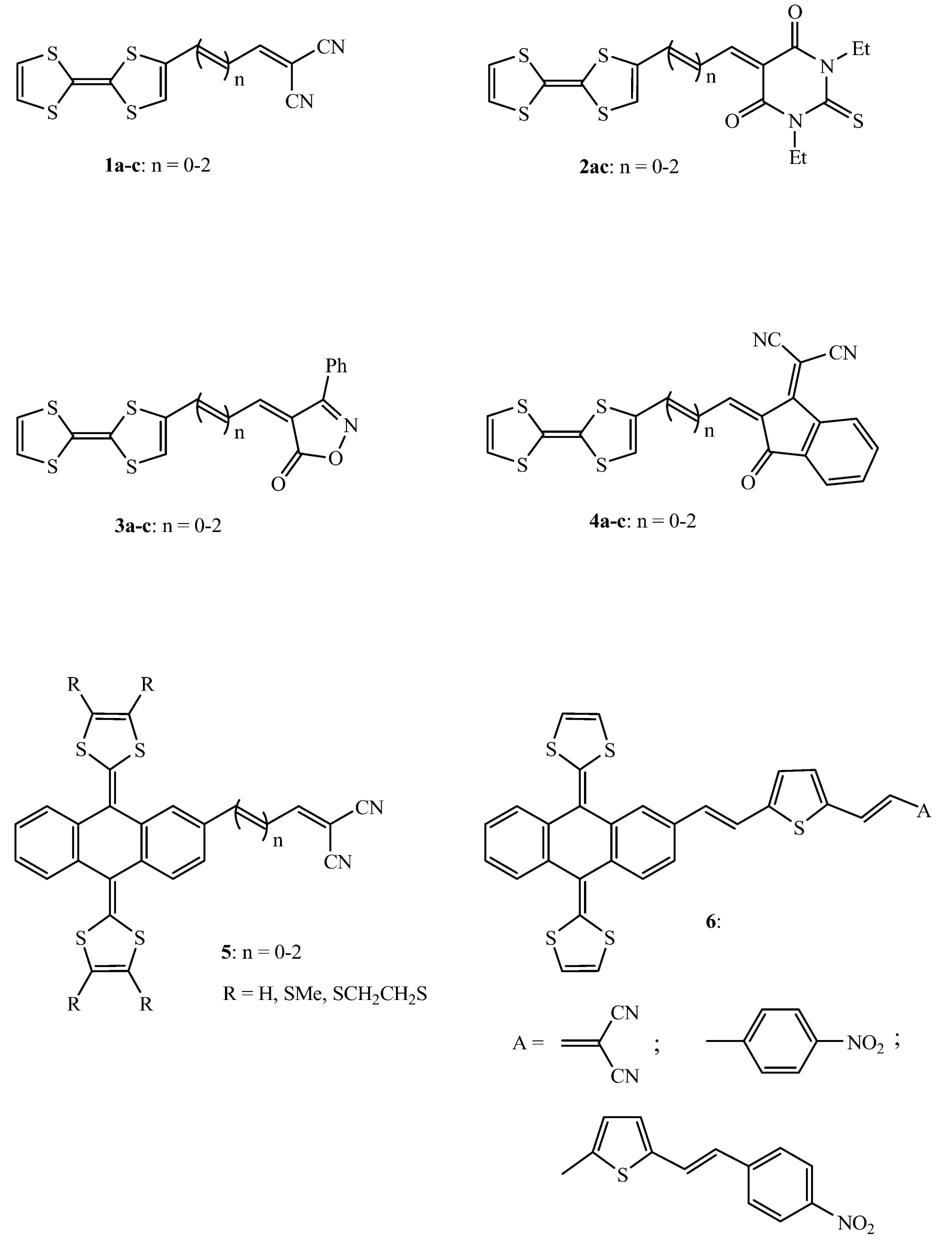
CHART 1



by an order of magnitude by oxidation of the metal atom. Subsequent rereduction restores the original β value and the NLO properties.

Tetrathiafulvalene (TTF) is a strong electron donor molecule that is reversibly oxidized in two one-electron processes to form the radical cation ($TTF^{\cdot+}$) and dication (TTF^{2+}) species at relatively low oxidation potential values ($E^1_{1/2ox} = 0.37$ V; $E^2_{1/2ox} = 0.67$ V; in CH_2Cl_2 GC vs SCE).[5] Although TTF was originally obtained to be used as strong electron donor molecule in the preparation of electrically conducting salts and charge-transfer complexes,[6] recently this outstanding redox-active molecule has found important applications in different fields.[7]

We have recently proved the usefulness of tetrathiafulvalene (TTF) and π-extended TTFs as NLO-phores and different TTF-based push–pull chromophores (**1**–**4**) have been synthesized and their electrochemical and NLO properties studied.[8] π-Extended TTFs have also proven to be efficient NLO-phores, and some D–π–A compounds (**5**, **6**) have been studied.[9] (Chart 1)

The combination of the inherent redox properties of TTF and its derivatives with different π-conjugated electron acceptors is an interesting approach for the molecular engineering of switchable NLO materials.[10] In this paper we describe the first example of TTF- and exTTF-based D–π–A systems bearing a tricarbonyl(η^6-arene)chromium complex as the acceptor moiety, in

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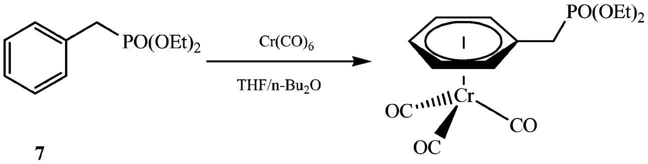
which the length of the conjugated bridge has been systematically increased. It is worth mentioning that these complex systems are constituted by two redox active units (TTF and chromium complex) able to act as switches for the NLO properties.

The novel compounds have been studied by cyclic voltammetry in order to determine their electrochemical behavior, and their structural and electronic properties have been calculated at ab initio Hartree–Fock and density functional theory levels. Finally, the NLO behavior was measured by using the EFISH (electric field-induced second harmonic generation) technique.

Results and Discussion

Synthesis. The preparation of TTF–π–Cr(0) complexes **12a–c** was carried out by Wittig–Horner reaction of the formyl-containing TTF **9a–c**[8c] with the $Cr(CO)_3$-complexed benzylphosphonate **8** as depicted in Scheme 1. As it is known, the Wittig–Horner reaction is among the most reliable and useful olefination processes in organic synthesis that allows for efficient control of the configuration of the generated double bond.[11] An important consequence of the selected starting compounds **8** and **9a–c** is the ability of tricarbonyl chromium arene complexes to stabilize benzylic anions,[12] and, therefore, the stabilized $Cr(CO)_3$-complexed benzyl phosphonate **8** should react stereoselectively with aldehydes **9a–c** affording complexes **12a–c** in an all-trans configuration.



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8

Thus, the reaction of phosphonate **8**[13] with formyl-TTFs **9a–c**, which were in turn prepared by a modification of our previous methods,[8,14] led after flash chromatography to the novel complexes **12a–c** as high-melting-point, stable, brown and red solids in moderate to good yields (46–69%). It is important to note that the Wittig–Horner reaction was carried out by using equimolar amounts of **8** and **9a–c** in THF as a solvent and potassium *tert*-butoxide as a base under an argon atmosphere. Previous attempts from **9a** using sodium hydride (60 and 95%) as a base at room temperature or under reflux led to complex **12a** in significantly poorer yields together with a small amount of compound **13** resulting from the loss of the $Cr(CO)_3$ moiety, which was characterized by comparison with a sample prepared by an alternative route.[15]

The ^{1}H NMR spectra of **12a–c** confirmed the all-trans configuration of the new compounds with vicinal coupling constants of around 15.5 Hz (see Experimental Section). In addition, these TTF–chromiumcarbonyl complexes were easily identified due to the characteristic signals of the 1,3-dithiole protons, which appear as two singlets at $\delta = 6.8$ (1H) and $\delta = 6.66$ (2H), and the upfield shifted arene protons of the chromoarene moiety. The typical carbonyl resonances of the CO ligands appear between $\delta = 234.4$ and 235.0. These carbonyl resonances have been used as a measure of the relative electron density on the metal center (increasing the electron richness with the downfield shift).[16] These are weak effects since no net charges are involved. However, they give a qualitative measure of the electron density on the chromium atom provided that the TTF unit acts as an electron donor that interacts electronically with the chromiumcarbonyl complex through the π-conjugated alkenyl bridge. The found δ values for the CO ligands are in full agreement with other related systems bearing a ferrocene as electron donor unit (δ 234.5–234.8).[17]

To determine the impact that the separation of the two dithiole rings of TTF has on the electronic properties of the D–π–A chromium complexes, we have carried out the synthesis of novel compounds **16a–c** in which the exTTF electron donor unit is covalently connected to the chromiumcarbonyl complex through an alkenyl bridge of variable length (Scheme 2).

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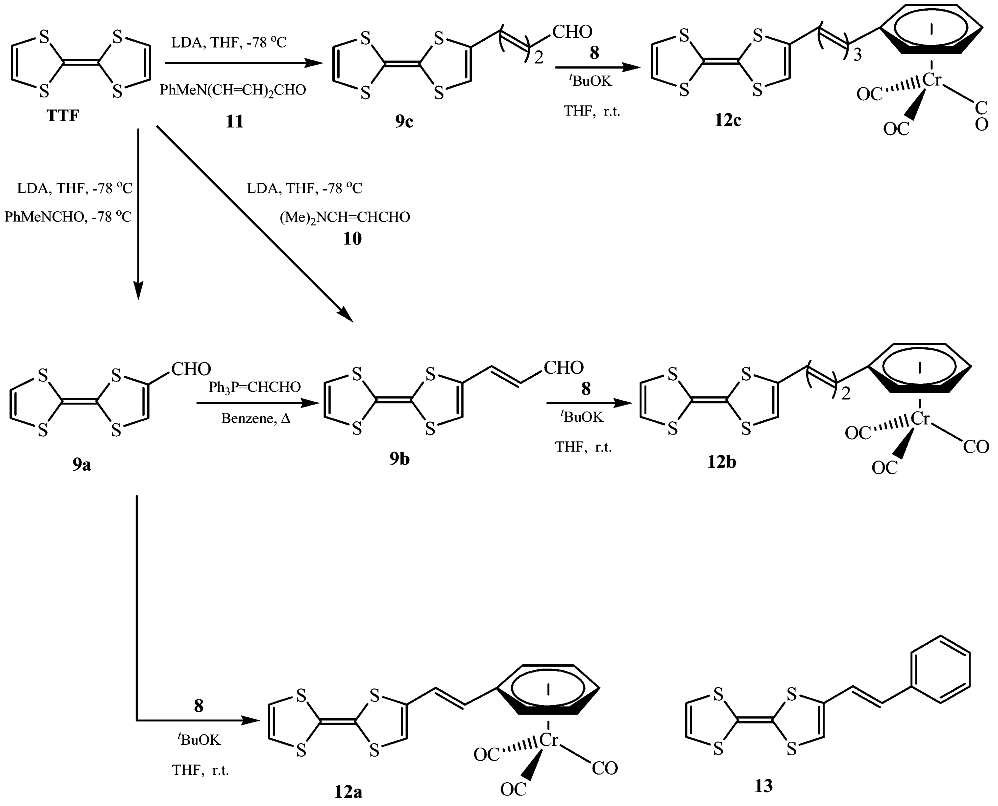
SCHEME 1



The synthesis of the target molecules **16a**–**c** was carried out from the respective aldehydes **15a**–**c**,[18] which were in turn prepared from commercially available 2-hydroxymethyl-9,10-anthraquinone **14** in a multistep synthetic procedure by Wittig–Horner reaction with Cr(CO)$_3$-complexed benzyl phosphonate **8** under conditions similar to those used for the preparation of **12a**–**c** (^{t}BuOK, THF, rt). Compounds **16a**–**c** were obtained as stable, high-melting-point solids (mp > 320 °C) in moderate to good yields (43–68%).

The ^{1}H NMR spectra of these compounds **16a**–**c** are rather complex to analyze due to the high number of protons linked to Csp^2 atoms (see Experimental Section). However, in some cases it was possible to observe the vinyl coupling constants of around 16 Hz, thus confirming the all-trans configuration for systems **16a**–**c**. Similarly to **12a**–**c**, compounds **16a**–**c** show the carbonyl resonances of the CO ligands at δ 234.6–235.1, thus confirming the electronic interaction of the exTTF donor unit with the chromoarene complex.

The electronic spectra of compounds **12a**–**c** as well as compounds **16a**–**c** show a strong band at low energies corresponding to a charge-transfer process from the donor moiety (TTF or exTTF, respectively) to the acceptor tricarbonylchromium arene moiety. The presence of the chromoarene unit in compounds **12** or in compounds **16** leads to a hipsochromic effect in the UV–vis spectra in comparison with their respective formyl-containig precursors (**9a**–**c**, **15a**–**c**). These findings could be accounted for by the poorer electron-accepting ability of the tricarbonylchromium arene unit compared to the formyl group. On the other hand, the increasing of the number of vinylene units between the donor and acceptor electroactive groups produces a remarkable bathochromic effect (**16a**, 441 nm; **16b**, 445 nm; **16c**, 457 nm in CH$_2$Cl$_2$) (Figure 1). Finally, the λ_{max} values determined for compounds **12a**–**c** and **16a**–**c** are not significantly influenced by the solvent polarity (Figure 2).

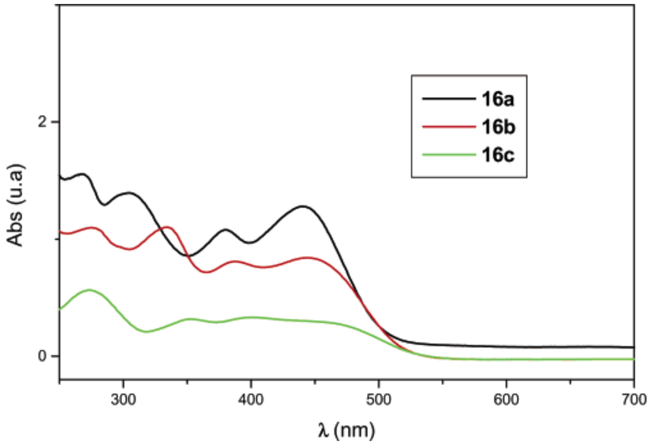


FIGURE 1. UV–vis spectra of **16a**–**c** in CH$_2$Cl$_2$.

Electrochemistry. The redox potentials of the novel TTF-based complexes **12a**–**c** and **16a**–**c** have been determined by cyclic voltammetry at room temperature in acetonitrile solutions, using a glassy carbon electrode as the working electrode, Ag/Ag$^+$ as a reference, and tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte. The redox potential values are collected in

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SCHEME 2

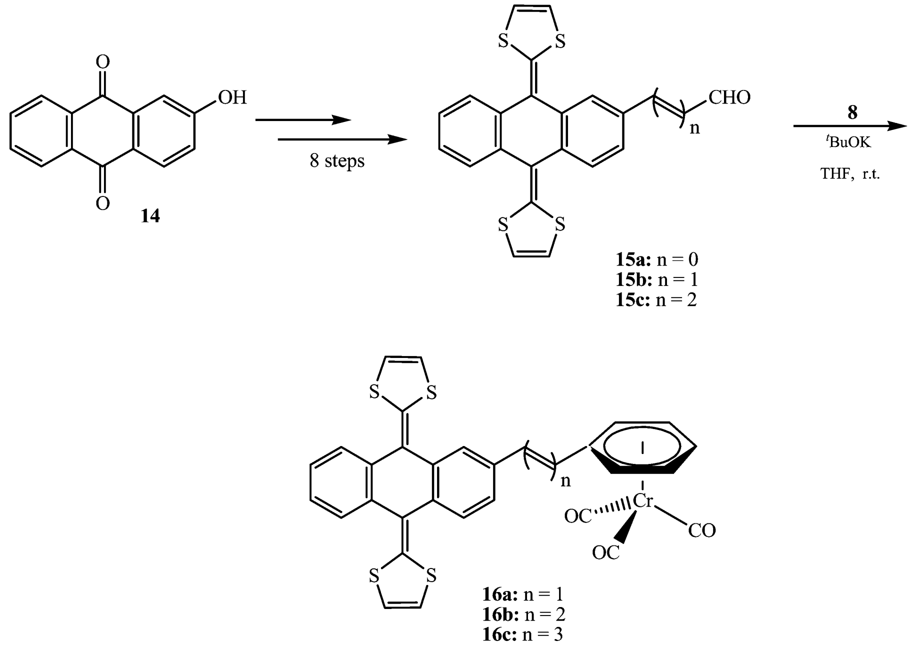

TABLE 1. Redox Potential Values (±0.01 V) for Compounds 12a−c and 16a−c (V vs Ag/Ag$^+$)

compd	$E^1_{1/2\mathrm{ox}}$	$E^2_{1/2\mathrm{ox}}$	E_{pa}	$E^1_{1/2\mathrm{red}}$	$E^1_{\mathrm{red,\,pc}}$	$E^2_{\mathrm{red,\,pc}}$
TTF	0.36	0.74				
8	0.90[a]				−1.60	
13	0.36	0.70				
12a	0.43	0.71			−1.65	
12b	0.42	0.75			−1.51	−1.66
12c	0.41	0.74			−1.51	−1.76
exTTF	0.29 (2e)					
16a	0.30 (2e)	0.74[a]			−1.66	
16b	0.30 (2e)	0.76[a]		−1.55	−0.84	
16c	0.29 (2e)	0.69[a]		−1.45	−0.82	

[a] Anodic peak experimental conditions: CH_3CN as a solvent, GCE as a working electrode, Bu_4NClO_4 (0.1 M) as a supporting electrolyte; 100 mV s^{-1}.

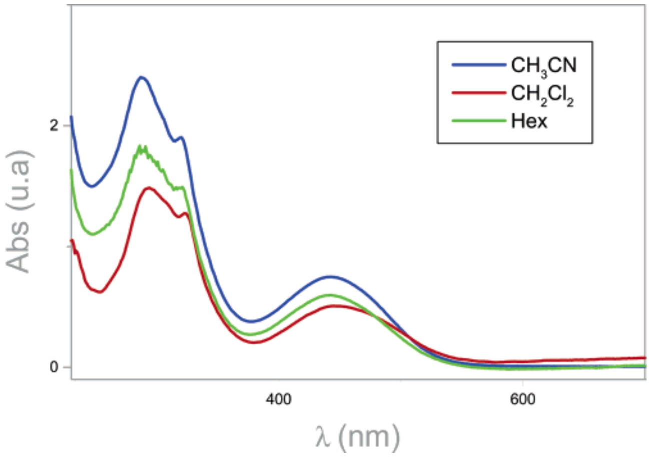

FIGURE 2. UV−vis spectra of **12a** in different solvents.

Table **1** together with the parent TTF and exTTF and phosphonate **8** for comparison purposes.

Compounds **12a**−**c** show two reversible one-electron oxidation waves at relatively low potential values corresponding to the formation of the radical cation (TTF$^{\bullet+}$) and dication (TTF^{2+}) species of the TTF moiety. These values are anodically shifted (70−50 mV) in comparison with the parent TTF measured under the same experimental conditions. This finding can be accounted for by the presence of the benzene−Cr(CO)$_3$ moiety acting as an acceptor moiety, and the distance between the D and A units. Increasing the number of vinylene units from **12a** to **12c** results in a decrease in the electronic interaction between the TTF and the chromium arene complex (see Table 1). This electronic interaction is confirmed by the CV of compound **13** resulting from the loss of the Cr(CO)$_3$ moiety. The first oxidation potential value of **13** ($E^1_{1/2\mathrm{ox}}$ = 0.36 V) is the same as that of the parent TTF, thus showing the strong impact that the presence of the Cr(CO)$_3$ unit has on the first oxidation potential values of **12a**−**c**.

This behavior is not observed for compounds **16a**−**c**, which exhibit only one quasireversible oxidation wave involving two electrons to form the dication exTTF^{2+} species,[19] at practically the same values as that observed for the parent exTTF molecule [9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene].[20] This result can be accounted for by considering the remarkably longer distance between the dithiole and the benzene−Cr(CO)$_3$ units in compounds **16a**−**c** related to compounds **12a**−**c** and confirms the observed behavior in the UV−vis spectra.

All voltammograms of compounds **12a**−**c** and **16a**−**c** show the presence of an irreversible reduction wave at around −1.5 or −1.6 V corresponding to the reduction of the benzene−Cr(CO)$_3$ moiety acting as electron acceptor. These values are in the same range than that observed for complex **8** (−1.60 V) and reveal the poor electron-accepting ability of the benzene−Cr(CO)$_3$ unit. In addition, compounds **16a**−**c** show an additional oxidation wave at around 0.7 V corresponding to the oxidation of the benzene−Cr(CO)$_3$ unit. This wave overlaps with the second oxidation wave of TTF in compounds **12a**−**c**

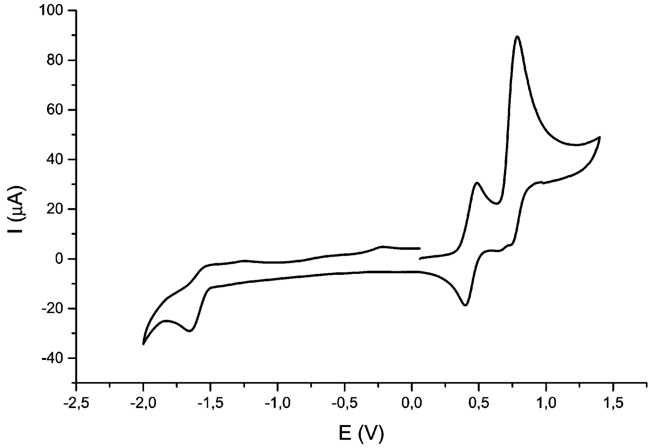

FIGURE 3. Cyclic voltammogram of **12a** in CH_2Cl_2. Experimental conditions: CH_3CN as solvent, GCE as working electrode, Bu_4NClO_4 (0.1 M) as supporting electrolyte; 100 mV s^{-1}.

(Figure 3), which is in agreement with that observed for reference compound **8** (see Table 1).

Theoretical Calculations and NLO Properties. The nonlinear optical properties of new chromophores **12a**–**c** and **16a**–**c** have been studied theoretically. The molecular geometry was first optimized using the B3P86/6-31G* model chemistry; the second-order nonlinear response was calculated using the *coupled perturbed Hartree–Fock* (CPHF) approach and the 6-31G* basis set due to the reliability achieved by this model chemistry (CPHF/6-31G*//B3P86/6-31G*) on a number of tetrathiafulvalene-derived NLO-phores.[8e] Excitation energies and excited-state properties were evaluated by the *time-dependent density functional theory* (TD-DFT) method. Although this methodology fails to accurately reproduce charge-transfer transitions, it is the best method that can be applied at a reasonable computational cost for medium-sized molecules and is known to reproduce quite accurately most of the electronic transitions of TTF derivatives.[21] In analogy to previous reports on the geometry of tetrathiafulvalene derivatives, compounds **12** display a boatlike TTF geometry,[22] while extended tetrathiafulvalenes **16** arrange on a butterfly like shape.[9,18,19a,20b] There are, however, two possible conformations depending on the relative arrangement of the dithiole rings and the chromium atom in **12** and **16** (see Figure 4). In conformation **a**, dithiole rings and tricarbonyl group are placed on the same side of the molecule, while in conformer **b** the dithiole groups arrange to keep far from the metal atom.

The B3P86/6-31G*-calculated energies for conformers **a** and **b** are very similar in every compound with differences below 0.3 kcal/mol. There are, however, differences in the calculated ground-state dipole moments that are larger for conformers **b** (6.12–7.69 D) compared to **a** (4.03–4.90 D) due to the additive effect of donor and acceptor groups in the **b** arrangement. Although calculations on both conformations lead to analogous qualitative conclusions, the following discussions describe the results obtained on the more polar **b** conformations provided that these must be favored at the high electric fields employed during the EFISH measurements.

The results of these calculations shown in Table 2 agree with previous reports[23] on chromium carbonyl arene complexes that concluded that the second-order nonlinear optical properties were mainly due to an intraligand charge-transfer transition (ILCT), but there is also a metal to ligand charge-transfer transition (MLCT) that affects the nonlinear response.

According to our calculations, the lowest energy absorption predicted at 2.04–2.48 eV corresponds in every case to a transition from the HOMO located on the tetrathiafulvalene moiety to the LUMO, which corresponds mainly to an antibonding π orbital on the ethylenic spacer (see Figure 5).

The second lowest energy absorption (calculated at 2.66–3.09 eV) band is due in every case to a transition from the HOMO-1 having an important contribution from the chromium d orbitals to the LUMO.

The charge-transfer processes associated to these electronic transitions can be explained on the basis of the topology of the orbitals involved. The HOMO→LUMO transition causes a charge transfer from TTF to the ethylenic bridge, while the HOMO-1→LUMO is associated with a transfer from the chromium atom to the bridge; thus, the nonlinear optical response associated with this transition is opposed to that of the HOMO→LUMO one. This effect can be best visualized by looking at the dipole moments of the ground and excited states of this compound (Figure 6). The ground-state dipole moment direction is mainly determined by the polarization of the tricarbonyl(benzene) chromium moiety from the benzene ring to the carbonyl groups

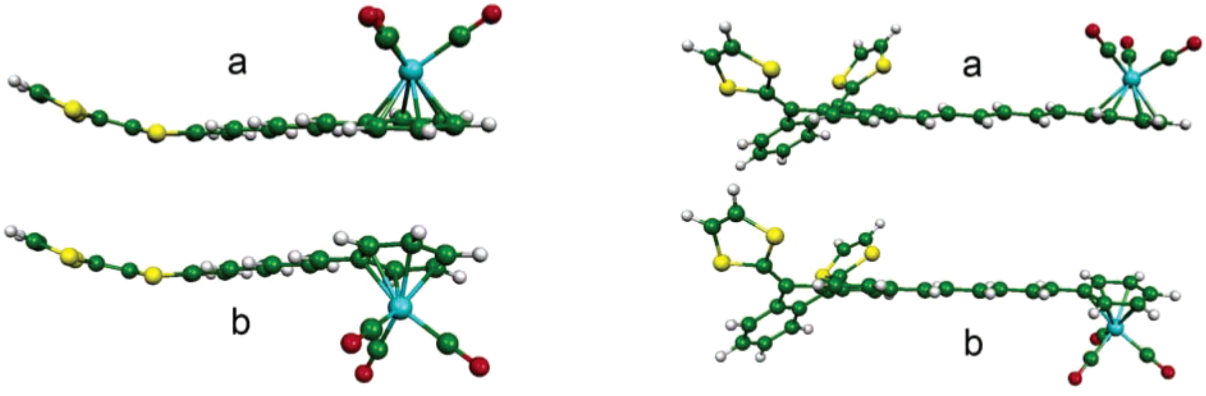

FIGURE 4. Different conformations calculated for compounds **12c** (left) and **16c** (right).

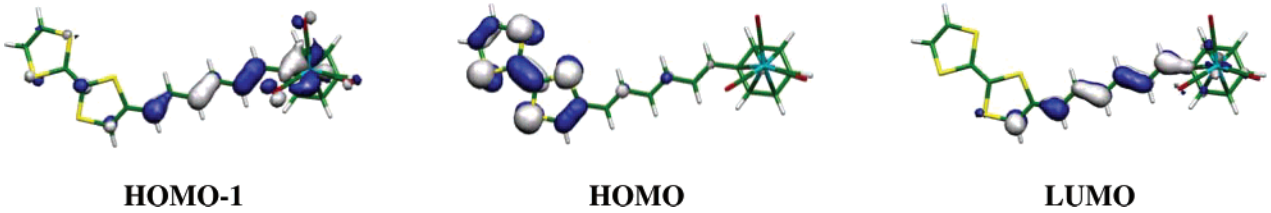

FIGURE 5. Molecular orbital topology calculated for **12c**.

TABLE 2. Theoretically Calculated Nonlinear Optical Properties of New Chromophores

	CPHF/6-31G*//B3P86/6-31G*				TD-B3P86/6-31G*				
compd	$\mu_g{}^a$	$\beta_{tot}(0)^b$	$\mu\beta(0)^c$	θ^d	transition	E^e	f_{os}	$\mu_g{}^a$	$\mu_e{}^a$
12a	6.36	7.7	−32.6	132.0	HOMO→LUMO	2.36	0.15	6.12	24.66
					HOMO-1→LUMO	3.09	0.21		6.89
12b	6.38	11.82	−45.0	126.7	HOMO→LUMO	2.17	0.21	6.17	28.51
					HOMO-1→LUMO	2.92	0.43		9.95
12c	6.43	17.4	−48.5	115.8	HOMO→LUMO	2.04	0.29	6.26	32.56
					HOMO-1→LUMO	2.78	0.68		12.63
16a	7.08	7.8	1.6	88.3	HOMO→LUMO	2.48	0.23	7.25	24.27
					HOMO-1→LUMO	2.94	0.24		5.31
16b	7.30	14.2	19.1	79.4	HOMO→LUMO	2.32	0.28	7.54	30.14
					HOMO-1→LUMO	2.79	0.62		12.24
16c	7.39	23.22	36.7	77.4	HOMO→LUMO	2.19	0.36	7.69	35.73
					HOMO-1→LUMO	2.66	0.98		14.02

[a] Debye. [b] 10^{-30} esu. [c] 10^{-48} esu. [d] Degrees (see text). [e] eV.

while the first excited-state dipole moment is determined by the charge transferred during the excitation and goes from the donor (TTF) to the acceptor (tricarbonyl(benzene) chromium) and the second excited-state dipole moment goes from the tricarbonyl chromium moiety to the TTF ring.

It is worth noting the large angles (θ) formed by the ground-state dipole moment and the vectorial hyperpolarizability, due mainly to the charge-transfer associated to the lowest energy absorption. The CPHF calculations show that while these molecules have large total hyperpolarizabilities (β_{tot}), the large angle (θ) above 90° gives rise to low negative $\mu\beta(0)$ values since these are calculated as $\mu_g\beta_{tot}(0)\cos(\theta)$.

The hyperpolarizabilities determined by EFISH in CH_2Cl_2 are in good qualitative agreement with these theoretical calculations since the $\mu\beta$ value displayed by **12a** was nearly zero while **12c** displayed a negative value ($\mu\beta = -124 \text{ x } 10^{-48}$ esu with $\mu\beta(0) = -90 \text{ x } 10^{-48}$ esu).

Calculations on extended tetrathiafulvalenes **16a**−**c** give rise to a picture analogous to that obtained for **12a**−**c**; there are, however, some important differences due to the different topology of the HOMO-1 orbital (Figure 7).

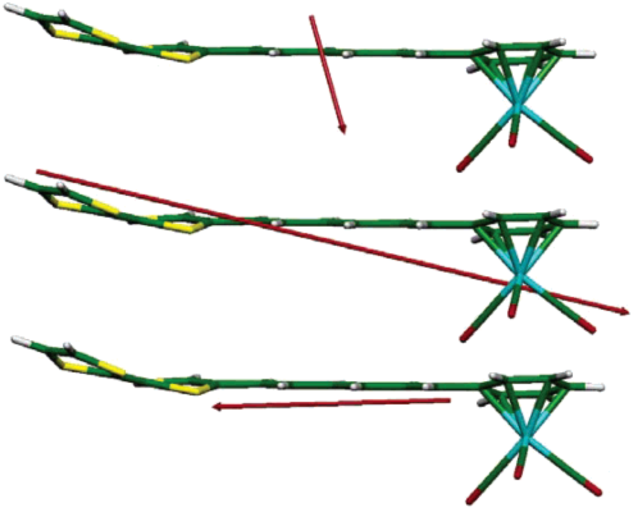

FIGURE 6. Calculated dipole moments of the ground and first and second excited states, respectively, of compounds **12c**.

In sharp contrast to compounds **12**, the HOMO-1 of **16** has an important contribution from one of the dithiole rings, and consequently the charge-transfer associated with the HOMO-1→LUMO transition is mainly directed from the extended tetrathiafulvalene to the ethylenic spacer. This can be observed in a more intuitive way looking at the graphic representation of the dipole moments shown in Figure 8.

It can be seen that the dipole moments of the first and second excited states have similar orientations, and hence the nonlinear optical effect associated with these states should be additive. In any case, the hyperpolarizability also forms a large angle with the ground-state dipole moment and the CPHF calculations predict low $\mu\beta(0)$ values, although in this case they are positive. There is also a good qualitative agreement with the EFISHG

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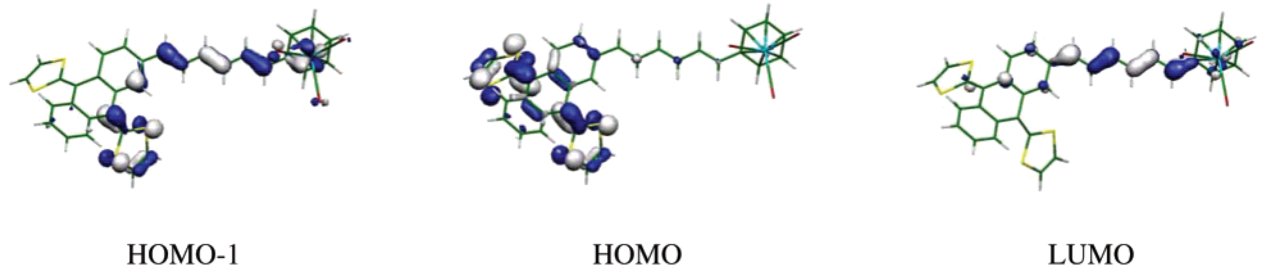

FIGURE 7. Molecular orbital topology calculated for **16c**.

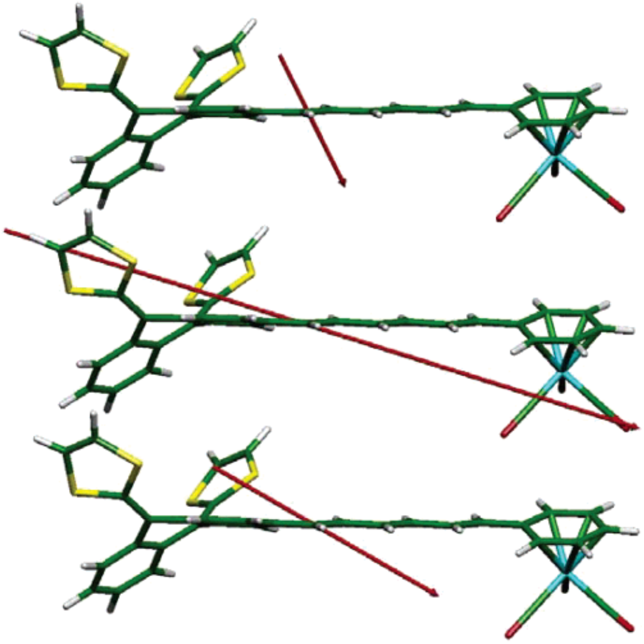

FIGURE 8. Calculated dipoles moments of the ground and first and second excited states, respectively, of compound **16c**.

measurements in CH_2Cl_2, which yielded a $\mu\beta$ value of 0 for **16a** and 97 ($\mu\beta(0) = 70$) for **16c**.

Conclusion

In summary, we have carried out the synthesis of a new series of D−π−A system in which strong electron donors (TTF and π-extended TTF) are covalently connected to a tricarbonyl (η^6-arene)chromium complex as the acceptor moiety through a systematically increased conjugated bridge of vinylene units. The cyclic voltammetry shows a significant influence of the tricarbonylchromium arene on the oxidation potentials of the TTF unit in compounds **12a**−**c**, and no remarkable effect is observed for exTTFs (**16a**−**c**). In agreement with these data, the electronic spectra of compounds **16a**−**c** show a simple additive effect of the vinylene units in going from **16a** to **16c**. The nonlinear optical properties of **12a**−**c** and **16a**−**c** have been calculated by using the ab initio CPHF/6-31G*//B3P86/6-31G* model, and the time-dependent density functional theory (TD-DFT) method has been used for the calculation of the electronic transitions. The calculations predict that an intraligand charge-transfer transition (ILCT) and the metal to ligand charge-transfer transition (MLCT) are responsible for the nonlinear response. In addition, the large angles formed by the ground-state dipole moment and the vectorial hyperpolarizability are responsible for the $\mu\beta$ values found experimentally by the EFISH technique.

Experimental Section

All melting points measured are uncorrected. IR spectra were recorded in KBr pellets. ^{13}C and ^{1}H NMR spectra were recorded at 300 and 75 MHz, respectively; chemical shifts are given as δ values (internal standard: TMS). The fundamental light at 1.907 μm was the first Stokes peak of a hydrogen Raman cell pumped by the 1.064 μm light from a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns, pulse). That light was passed through a linear polarizer and focused on the EFISH cell. The polarizing dc voltage (parallel to the light polarization) used in this cell was 6 kV. The output light from the cell was passed through an interference filter to select the second harmonic light (0.954 μm), which was finally detected with a R642 photomultiplier from Hamamatsu. Static $\mu\beta(0)$ values were deduced from the experimental values using a two-level dispersion model. Cyclic voltammograms were recorded on a potentiostat/galvanostat equipped with a software electrochemical analysis Model 250 by using a GCE (glassy carbon) electrode as working electrode, an SCE as a reference electrode, $Bu_4N^+ClO_4$ as a supporting electrolyte, and dichloromethane as a solvent and at scan rate of 200 mV/s. Tetrathiafulvalene (TTF), lithium diisopropylamide (LDA), hexacarbonyl chromium, *N*,*N*-dimethylaminoacroleine, and triphenylphosphoranylideneacetaldehyde were used without further purification. Diethyl ether and tetrahydrofuran were dried with sodium and distilled before use. Theoretical calculations were performed with the Gaussian 98 and Gaussian 03 programs.[24] Geometry optimizations were performed on isolated entities using the default convergence criteria, and molecular hyperpolarizabilities were calculated analytically using the CPHF procedure.

2-Formyltetrathiafulvalene (9a)[8c] and (*E*)-3-(Tetrathiafulvalenyl)acrylaldehyde (9b):[8c] Prepared by following the methods previously reported in the literature.

5-(Tetrathiafulvalenyl)penta-2,4-dien-1-al (9c). Under an argon atmosphere, at −78 °C, 0.73 mL (1.09 mmol) of a 1.5 M solution of lithium diisopropylamide (LDA) in tetrahydro-

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[24] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

furan/heptane was added to a solution of 204 mg (1.0 mmol) of TTF in 10 mL of dry THF. Then, 281 mg (1.0 mmol) of 5-(*N*-methyl-*N*-phenylamino)-2,4-pentadienal[8c] **11** was added, and the reaction was allowed to reach room temperature overnight. Afterward, the mixture was poured over a 2 M aqueous solution of hydrochloric acid. The organic layer was extracted with dichoromethane and dried over sodium sulfate. After vacuum elimination of the solvent, the residue obtained was chromatographed (hexane/dichloromethane) to yield 136 mg (48%) of **9c** as a red solid: mp 151−152 °C; ^{1}H NMR (CDCl$_3$ 300 MHz) δ 9.59 (d, J = 7.8 Hz, 1H), 7.12 (dd, J = 15.3, 11.4 Hz, 1H), 6.75 (d, J = 15.3 Hz, 1H), 6.61 (s, 1H), 6.35 (s, 2H), 6.27 (dd, J = 14.7, 11.4 Hz 1H), 6.22 (dd, J = 14.7, 7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 193.1, 150.4, 135.2, 132.3, 131.9, 128.7, 125.1, 119.1, 118.9, 114.1, 106.1; FTIR (KBr, cm^{-1}) 1660, 1605, 1582, 1504, 114, 1160; UV−vis (CH$_2$Cl$_2$) λ_{max} (nm) 520, 334; MS *m*/*z* (rel intensity) 284 (M$^+$, 100). Anal. Calcd for $C_{11}H_8OS_4$: C, 46.49; H, 2.84. Found: C, 46.82; H, 2.97.

2-Formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15a),[18] 2-(*E*)-2-Formylvinyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15b),[18] 2-(4-Formylvinyl-1,3-butadienyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15c),[18] and Tricarbonyl (η^6-diethylbenzylphosphonate)chromium(0) (8):[18] Prepared by following the methods previously reported in the literature.

Synthesis of TTF Derivatives 12a−c and 16a−c: General Procedure. To a degassed solution of phosphonate complex **8** (1.0 mmol) in dry THF (10 mL), 1.1 mmol of *tert*-BuOK was added under argon. After stirring the mixture for 10 min at rt, 1.0 mmol of the corresponding formyl-TTF derivative (**9a**−**c**, **15a**−**c**) in 2 mL of THF was added to the suspension. The reaction mixture was stirred at room temperature for 0.5 h. After this time, the solvent was removed in vacuo and the final product was purified by flash chromatography by using hexane/ethyl acetate as an eluent.

Tricarbonyl {η^6-[(*E*)-2-(2-Tetrathiafulvalenyl)ethenyl]benzene}chromium(0) (12a). By following the above general procedure and using formyl-TTF **9a** as the reagent, derivative **12a** was obtained in a 69% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 7.20 (d, J = 15.8 Hz, 1H), 6.89 (s, 1H), 6.66 (s, 2H), 6.12(d, J = 15.9 Hz, 1H), 5.95 (d, J = 6.30 Hz, 2H), 5.74 (t, J = 6.45 Hz, 2H), 5.62 (t, J = 6.3 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 234.4, 135.4, 128.6, 123.5, 123.2, 120.4, 120.3, 113.9, 107.5, 106.6, 94.9, 93.8, 93.00; FTIR (KBr, cm^{-1}) 3074, 2924, 2853, 1973, 1954, 1886, 1869, 1618, 658, 646, 629; UV−vis (CH$_2$Cl$_2$) λ_{max} (nm) 449, 325, 294, 227; UV−vis (C$_6$H$_{14}$) λ_{max} (nm) 441, 321, 289, 221; UV−vis (CH$_3$CN) λ_{max} (nm) 441, 320, 288, 219; UV−vis (MeOH) λ_{max} (nm) 447, 322, 276; MS *m*/*z* 442, 358, 332, 306, 261, 230, 178, 146, 128, 115, 12, 88, 76. Anal. Calcd for $C_{17}H_{10}CrO_3S_4$: C, 46.14; H, 2.28; S, 28.98. Found: C, 46.45; H, 2.53; S, 28.88.

Tricarbonyl {η^6-[(*E*,*E*)-4-(2-Tetrathiafulvalenyl)-1,3-butadienyl]benzene}chromium(0) (12b). By following the above general procedure and using (*E*)-3-(tetrathiafulvalenyl)-acrylaldehyde (**9b**) as the reagent, derivative **12b** was obtained in a 68% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 6.98 (dd, J_1 = 15.4 Hz, J_2 = 10.4 Hz, 1H), 6.81 (s, 1H), 6.71 (d, J = 15.4 Hz, 1H), 6.66 (s, 2H), 6.46 (d, J = 15.5 Hz, 1H), 6.27 (dd, J_1 = 15.1 Hz, J_2 = 10.5 Hz, 1H), 5.87 (d, J = 6.3 Hz, 2H), 5.72 (t, J = 6.5 Hz, 2H), 5.60 (t, J = 6.2 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 235.0, 136.4, 132.2, 131.8, 131.6, 127.2, 122.2, 120.8, 120.7, 113.9, 108.6, 107.9, 95.4, 94.2, 93.5; FTIR (KBr, cm^{-1}) 3080, 2924, 2855, 1956, 1877, 1859, 1618, 974, 656, 631; UV−Vis (CH$_2$Cl$_2$) λ_{max} (nm) 462, 327, 316, 228; UV−vis (C$_6$H$_{14}$) λ_{max} (nm) 450, 324, 311, 221; UV−vis (CH$_3$CN) λ_{max} (nm) 453, 323, 311, 218; UV−vis (MeOH) λ_{max} (nm) 461, 325, 278; MS *m*/*z* 468, 384, 358, 332, 230, 210, 185, 166, 153, 152, 148, 147, 146, 115, 102, 88, 76. Anal. Calcd for $C_{19}H_{12}CrO_3S_4$: C, 48.70; H, 2.58; S, 27.37. Found: C, 48.73; H, 2.96; S, 27.19.

Tricarbonyl {η^6-[(*E*,*E*,*E*)-6-(2-Tetrathiafulvalenyl)-1,3,5-hexatrienyl]benzene}chromium(0) (12c). By following the above general procedure and using 5-(tetrathiafulvalenyl)-penta-2,4-dien-1-al (**9c**) as the reagent, derivative **12c** was obtained in a 46% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 7.10−6.96 (m, 2H), 6.75 (s, 1H), 6.66 (s, 2H), 6.64 (d, J = 15.0 Hz, 1H), 6.58 (dd, J_1 = 14.2 Hz, J_2 = 9.9 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 6.24 (dd, J_1 = 15.3 Hz, J_2 = 9.7 Hz, 1H), 5.88 (d, J = 6.2 Hz, 2H), 5.72 (t, J = 6.5 Hz, 2H), 5.59 (t, J = 6.2 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 234.6, 136.4, 135.3, 134.6, 132.6, 132.2, 130.1, 125.9, 121.0, 120.4, 120.3, 118.6, 107.9, 107.7, 95.0, 93.7, 93.0; FTIR (KBr, cm^{-1}) 3080, 3020, 2924, 2853, 1956, 1882, 1857, 1618, 988, 654, 631; UV−vis (CH$_2$Cl$_2$) λ_{max} (nm) 456, 349, 339, 228; UV−vis (C$_6$H$_{14}$) λ_{max} (nm) 442, 345, 332, 217; UV−vis (CH$_3$CN) λ_{max} (nm) 452, 346, 335, 218; UV−vis (MeOH) λ_{max} (nm) 453, 346, 267; MS *m*/*z* 494, 360, 359, 358, 230, 179, 178, 165, 148, 146, 115, 102, 76. Anal. Calcd for $C_{21}H_{14}CrO_3S_4$: C, 51.00; H, 2.85; S, 25.93. Found: C, 50.91; H, 3.16; S, 25.63.

Tricarbonyl {η^6-[(*E*)-2-(2-(9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl)ethenyl]benzene}chromium-(0) (16a). By following the above general procedure and using 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **15a** as the reagent, derivative **16a** was obtained in a 68% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 7.91 (d, J = 1.6 Hz, 1H), 7.76−7.71 (m, 3H), 7.58 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 7.40−7.35 (m, 3H), 7.00 (d, J = 16.3 Hz, 1H), 6.66−6.63 (m, 4H), 6.02 (d, J = 6.2 Hz, 2H), 5.79 (t, J = 6.6 Hz, 2H), 5.62 (t, J = 6.3 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 235.1, 137.2, 136.8, 136.6, 135.4, 131.9, 127.4, 126.7, 126.6, 126.3, 126.2, 125.9, 124.6, 122.5, 122.4, 119.0, 118.9, 118.8, 108.6, 95.7, 93.9, 93.3; FTIR (KBr, cm^{-1}) 3080, 3021, 2926, 2855, 1963, 1882, 1686, 989, 658, 631; UV−vis (CH$_2$Cl$_2$) λ_{max} (nm) 441, 380, 304, 267; UV−vis (C$_6$H$_{14}$) λ_{max} (nm) 436, 378, 299, 268; UV−vis (CH$_3$CN) λ_{max} (nm) 435, 376, 305, 267; UV−vis (MeOH) λ_{max} (nm) 434, 377, 271; MS *m*/*z* 618, 534, 484, 483, 482, 380, 321, 278, 241. Anal. Calcd for $C_{31}H_{18}CrO_3S_4$: C, 60.18; H, 2.93; S, 20.73. Found: C, 59.95; H, 3.10; S, 20.62.

Tricarbonyl {η^6-[(*E*,*E*)-4-(2-(9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl)-1,3-butadienyl]benzene}chromium(0) (16b). By following the above general procedure and using 2-(*E*)-formylvinyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **15b** as the reagent, derivative **16b** was obtained in a 64% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 7.85 (d, J = 1.7 Hz, 1H), 7.75−7.69 (m, 3H), 7.48 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.40−7.34 (m, 2H), 7.21−7.06 (m, 2H), 6.87 (dd, J_1 = 14.9 Hz, J_2 = 4.4 Hz, 1H), 6.63 (s, 4H), 6.45 (dd, J_1 = 15.3 Hz, J_2 = 4.5 Hz, 1H), 5.92 (d, J = 6.6 Hz, 2H), 5.74 (t, J = 6.2 Hz, 2H), 5.60 (t, J = 6.2 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 234.7, 138.1, 137.2, 136.6, 136.4, 136.1, 135.7, 133.1, 130.3, 129.7, 127.4, 126.7, 126.3, 125.9, 124.1, 122.5, 119.0, 118.9, 108.4, 95.6, 94.1, 93.5; FTIR (KBr, cm^{-1}) 3069, 3020, 2924, 2853, 1960, 1888, 1618, 1543, 1508, 1456, 982, 656, 631; UV−vis (CH$_2$Cl$_2$) λ_{max} (nm) 445, 389, 335, 276; UV−vis (C$_6$H$_{14}$) λ_{max} (nm) 440, 383, 330, 277; UV−vis (CH$_3$CN) λ_{max} (nm) 444, 383, 331, 217; UV−vis (MeOH) λ_{max} (nm) 439, 383, 331; MS *m*/*z* 644, 534, 510, 509, 508, 303, 254, 220, 205, 149, 111, 97, 83, 80, 70, 72. Anal. Calcd for $C_{33}H_{20}CrO_3S_4$: C, 61.47; H, 3.13; S, 19.89. Found: C, 61.76; H, 3.22; S, 19.62.

Tricarbonyl {η^6-[(*E*,*E*,*E*)-6-(2-(9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl)-1,3,5-hexatrienyl]benzene}chromium(0) (16c). By following the above general procedure and using 2-(4-formyl-1,3-butadienyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **15c** as the reagent, derivative **16c** was obtained in a 43% yield: mp > 320 °C (dec); ^{1}H NMR ((CD$_3$)$_2$CO, 300 MHz) δ 7.81 (d, J = 1.7 Hz, 1H), 7.76−6.67 (m, 3H), 7.48−7.33 (m, 3H), 7.16−6.93 (m, 2H), 6.81−6.40 (m, 3H), 6.62 (s, 4H), 6.31 (dd, J_1 = 15.4 Hz, J_2 = 6.6 Hz, 1H), 5.86 (d, J = 6.3 Hz, 2H), 5.71 (t, J = 6.4 Hz, 2H), 5.57 (t, J = 6.2 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 234.6, 136.8, 136.7, 136.2, 136.0, 134.3, 133.8, 133.4, 133.1, 132.7, 132.6, 130.3, 130.1, 129.4, 129.3, 126.9, 126.2, 125.8, 125.2, 125.1, 123.6, 118.6, 118.4, 108.1, 95.0, 93.4, 92.8; FTIR (KBr, cm^{-1}) 3068, 3020, 2922, 2853, 1958, 1875, 1724, 1543, 1508, 1452, 1414, 995, 799, 756, 654, 629, 619; UV−vis (CH_2Cl_2) λ_{max} (nm) 457, 401, 352, 273; UV−vis (C_6H_{14}) λ_{max} (nm) 450, 394, 350; UV−vis (CH_3CN) λ_{max} (nm) 466, 394, 351, 270; UV−vis (MeOH) λ_{max} (nm) 448, 393, 350; MS *m/z* 670, 612, 560, 536, 535, 534, 532, 267, 207, 78, 69, 63. Anal. Calcd for $C_{35}H_{22}CrO_3S_4$: C, 62.67; H, 3.31; S, 19.12. Found: C, 62.73; H, 3.49; S, 18.89.

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