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Towards new organometallic second-order nonlinear optical materials

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Abstract

We report on the synthesis of new organometallic donor-acceptor molecules for second-order nonlinear optics. They contain ferrocene as the donor group, cyano or tricyano-derivatized furan as the acceptor, and thiophene or 3,3'-bipyridine derivatives as π -bridge. These chromophores can be functionalized, in order to incorporate them later in polymers, covalently or not. **To cite this article:** A.-L. Roy et al., C. R. Chimie 8 (2005).

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Résumé

Nous présentons la synthèse de nouveaux chromophores à transfert de charge unidimensionnel (*push-pull*) possédant un groupement donneur d'électrons de type organométallique (ferrocène). Ces chromophores sont fonctionnalisés ou non, afin de les incorporer à terme, de façon covalente ou non, au sein de polymères. **Pour citer cet article:** A.-L. Roy et al., C. R. Chimie 8 (2005).

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Mots clés: Organométallique; Chromophore; ONL; Ferrocène; Couplage de Suzuki; Synthèse convergente

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1. Introduction

Second-order nonlinear optical (NLO) polymeric materials have long been recognized as potential candidates for electro-optic applications [1]. The interest in these materials derives from their better processability and larger NLO responses than inorganic materials such as lithium niobate crystals (LiNbO_3), currently used in electro-optical modulators.

In order to exhibit second-order optical effects, these materials must have π electrons, which delocalize in response to an applied electric field, resulting in spatial asymmetry. At the molecular level, the second-order NLO properties (molecular hyperpolarizability (β)) arise from non centrosymmetric π -conjugated charge transfer molecules containing both electron-acceptor and electron-donor groups connected by an electron-transmitting bridge (push–pull structure, characterized by a large dipole moment, μ) [2]. The bulk second-order NLO response originates typically from noncentrosymmetric alignment of NLO chromophores in poled polymers [2].

Quantum mechanical analysis based on a simple two-level model [3] and the bond order alternation (BOA) principle [4] have provided useful structure/property relationships for the design of chromophores with ever improving β values. It has been shown (Chart. 1) that very large nonlinearities can be achieved by combining heterocyclic conjugating units such as thiophene with tricyano-derivatized furan electron-

acceptor [5], for example FTC chromophore **I** [6], or by employing extended polyene π -bridged systems with strong multicyno-containing heterocyclic electron-acceptor like CLD chromophore **II** [7].

Compared to organic nonlinear optics, the field of organometallic nonlinear optics is relatively less explored, even if organometallics are potentially interesting candidates for NLO purposes [8]. Indeed, they show very strong absorption bands [metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT)] in the UV–Vis region, which are related to high transition dipole moments and low transition energies. Among the metallocene systems that have been examined in detail from both experimental and theoretical perspectives, ferrocene-containing compounds have emerged [9]. Although the electron-donor ability of this group is moderate, comparable to *p*-methoxyphenyl group [9], it offers the possibility of the NLO properties redox switching as well as an easy introduction of chirality.

In previous papers, we described a series of organometallic push–pull chromophores [10] based on organometallic donors such as ferrocene [10a,e], thiophene conjugated spacers and either organic acceptors, such as benzonitrile [10b,d], or organometallic acceptors. Their syntheses relied on palladium-catalyzed cross-coupling reactions and conventional Wittig or Wittig–Horner reactions. We also described a novel class of NLO 6,6'-(disubstituted)-3,3'-bipyridine-based chromophores (such as chromophore **III**) [11]. The new

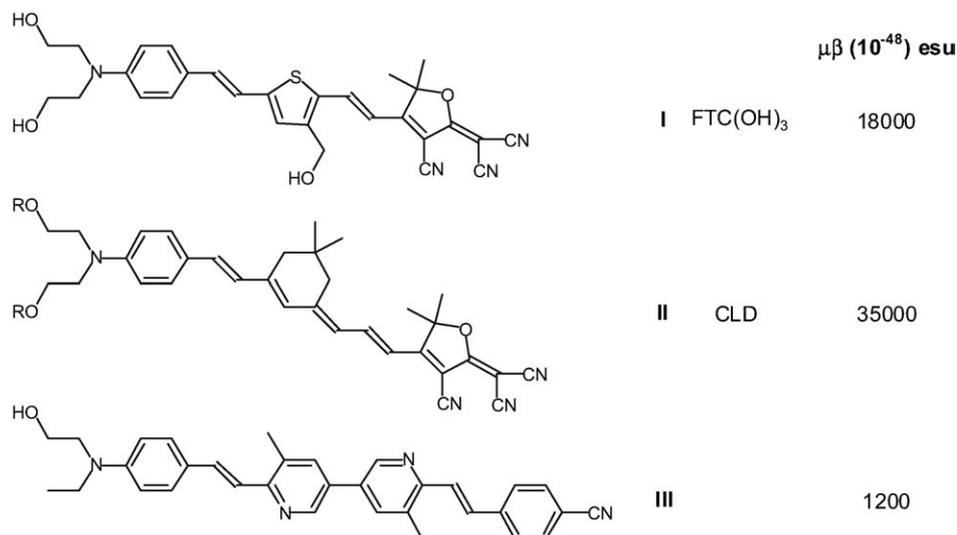


Chart. 1. Structure and properties of some π -conjugated chromophores.

large-scale and versatile strategy to access to these compounds is based on (i) the synthesis of a library of conjugated 6-substituted-3-bromopyridine building blocks, (ii) their transformation to 6-substituted-3-pyridylboronic ester building blocks, and (iii) the cross-coupling by the metal-catalyzed Suzuki reaction [12]. The main advantage of this synthetic pathway is the flexibility to combine ‘tailor-made’ building blocks, depending on the expected optical properties of the chromophore.

The present contribution reports on the synthesis of two new ferrocene-based chromophores **IV** and **V**, containing the same spacer and acceptor groups as chromophores **I** and **III**.

2. Results and discussion

The structures of the new π -conjugated organometallic chromophores (**IV**–**V**) are shown in Chart 2.

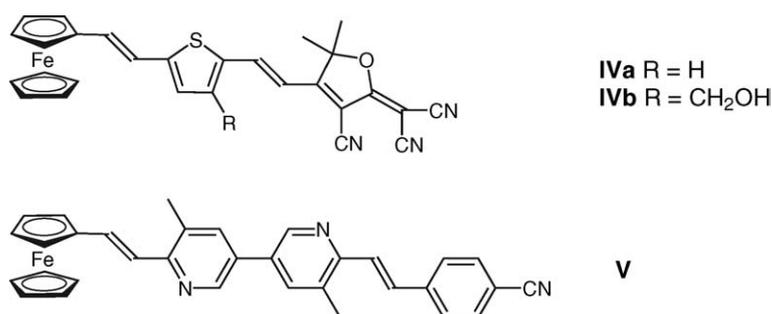
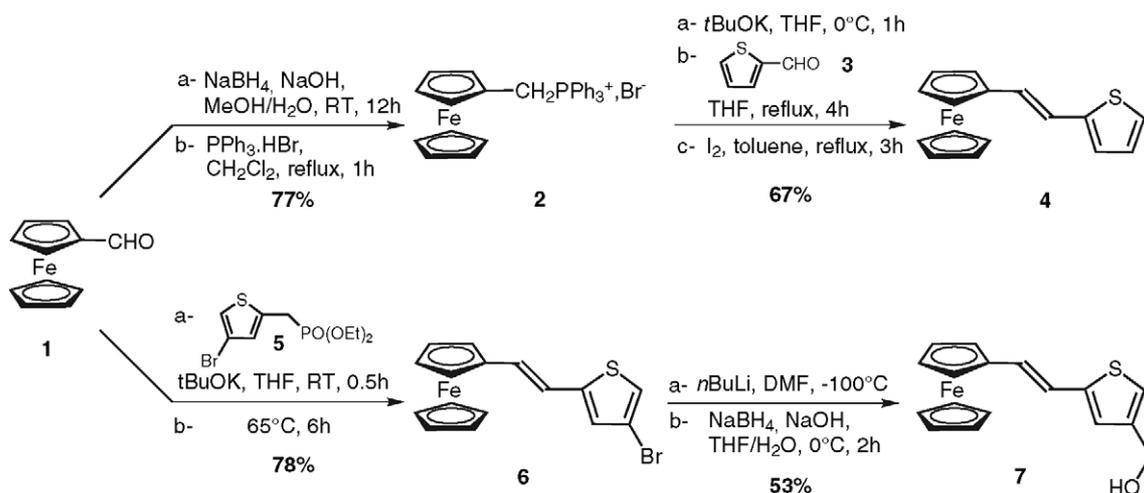


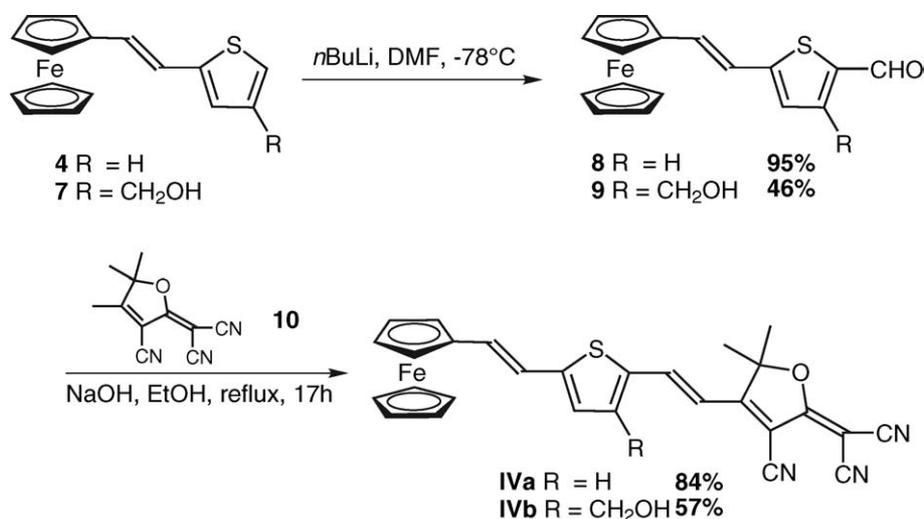
Chart 2. Structure of the newly-designed π -conjugated organometallic chromophores **IV** and **V**.



Scheme 1. Preparation of thiophene-based building blocks **4** and **7**.

The synthesis of the thiophene-based chromophores **IVa** and **IVb** is based on (i) a stereoselective access to the alkenes (*E*)-**4** and (*E*)-**7** as described in Scheme 1, (ii) a Knoevenagel condensation with the tricyanofuran acceptor **10** (Scheme 2).

Building block **4** was obtained via a Wittig condensation [13] between the organometallic phosphonium **2**, prepared following a described procedure [14], and commercially available thiophene carboxaldehyde (**3**). The alkene **4** was isolated as a 80:20 mixture of the two stereoisomers (*E*) and (*Z*), respectively. Their separation by chromatography was unsuccessful. However, isomerization of the minor (*Z*) product could be performed by heating the crude mixture in the presence of a catalytic amount of iodine, giving access to (*E*)-**4** [13] in 67% yield. Concerning the preparation of building block **7**, in which the thiophene ring is substituted by a hydroxymethyl side chain, a Wittig–Horner–Emmons

Scheme 2. Obtention of chromophores **IVa** and **IVb**.

condensation was chosen; indeed, this condensation is highly stereoselective. Starting material 4-bromothiophene-2-diethylphosphonate (**5**) was prepared as described in the literature [6]. Ferrocenecarboxaldehyde (**1**) was condensed with **5**, in the presence of *t*-BuOK, giving the alkene (*E*)-**6** in 78% yield after purification. No trace of the (*Z*) isomer was observed. ¹H NMR of alkenes **4** and **6** clearly indicate the *trans* nature of the double-bond, with coupling constants for the ethylene bridge signals of 15.9 and 16.0 Hz respectively. The hydroxymethyl side chain was introduced on **6** via a metal-halogen exchange/formylation/reduction sequence on the fourth position of the thiophene ring, giving compound **7** with a 53% overall yield.

Subsequent formylation of the fifth position of the thiophene ring gave the aldehydes **8** [13] and **9** which were reacted in basic conditions with the tricyanofuran acceptor **10**, prepared according to a described procedure [15], to afford the chromophores **IVa** and **IVb** in 84% and 57% yields respectively. Their spectroscopic data are consistent with the assigned structures¹.

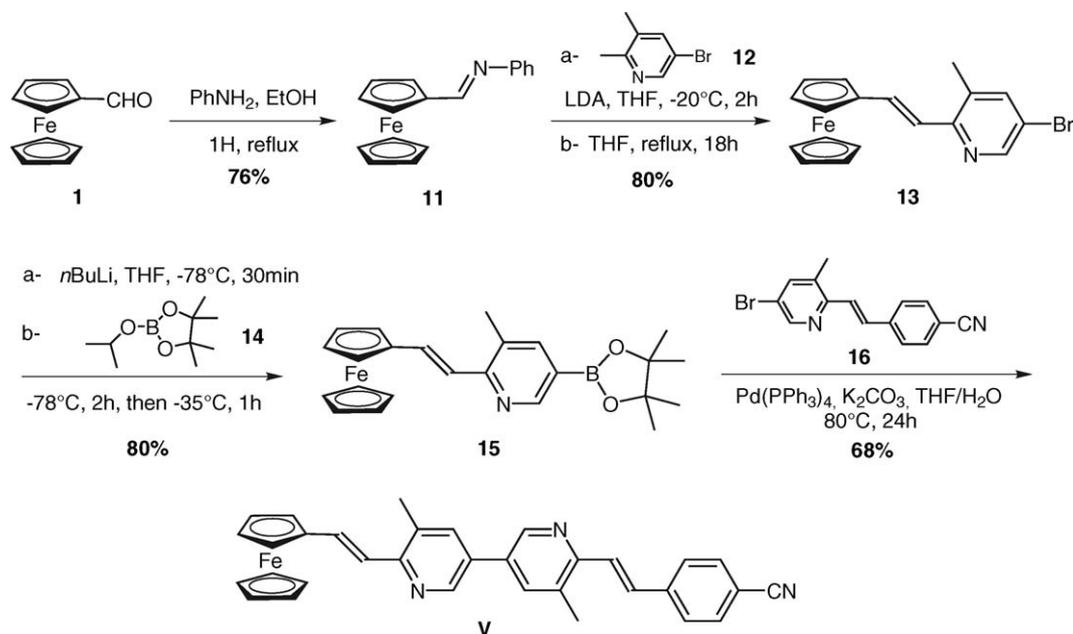
The synthetic approach to prepare chromophore **V** is based on the Suzuki coupling of a 6-substituted-3-

bromopyridine and a 6-substituted-3-pyridylboronic ester building blocks (Scheme 3). To access to these key intermediates, two different routes were used, depending on the electron-donor or the electron-acceptor character of the end-substituent.

Regarding brominated compound **13**, bearing an electron-rich aromatic ring, an adaptation of the Siegrist reaction was chosen [16]. The Siegrist method is a condensation between an aryl imine and the methyl group of an aromatic ring, in the presence of a base such as *t*-BuOK, allowing the stereoselective formation of *trans*-stilbene derivatives. First, condensation of the ferrocenecarboxaldehyde (**1**) with aniline in refluxing toluene afforded **11** in 76% yield after recrystallization in diethyl ether. Treatment of complex **11** with **12**, prepared as described previously [11a,b], in the presence of LDA, instead of *t*-BuOK, in THF at -20 °C gave **13** in 80% yield on a multigram scale. As expected, examination of the ¹H NMR spectra of the product showed that only the *trans*-isomer was obtained. Borylation of building block **13** was realized in 80% yield upon reaction with *n*-BuLi and commercially available 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **14**. The brominated building block bearing an electron-withdrawing group **16** was obtained in a reasonable yield (31%) from the one-step Knoevenagel type condensation reaction in acidic medium of *p*-cyanobenzaldehyde with **12** [12b]. **16** was coupled with the borylated building block **15**, under standard catalytic conditions, to give the new push-pull

¹ **IVa**: ¹H NMR (200 MHz, (CD₃)₂CO) δ (ppm): 7.75 (d, 1H, *J* = 15.8 Hz); 7.35 (d, 1H, *J* = 4.0 Hz); 7.00 (d, 1H, *J* = 15.8 Hz); 6.99 (d, 1H, *J* = 4.0 Hz); 6.79 (d, 1H, *J* = 15.8 Hz); 6.62 (d, 1H, *J* = 15.7 Hz); 4.51 (m, 2H); 4.44 (m, 2H); 4.18 (s, 5H); 1.75 (s, 6H).

IVb: ¹H NMR (200 MHz, (CD₃)₂CO) δ (ppm): 8.36 (d, 1H, *J* = 15.7 Hz); 7.18 (s, 1H); 7.14 (d, 1H, *J* = 15.9 Hz); 7.01 (d, 1H, *J* = 15.9 Hz); 6.76 (d, 1H, *J* = 15.7 Hz); 4.86 (d, 2H, *J* = 5.4 Hz); 4.65 (m, 2H); 4.45 (m, 2H); 4.19 (s, 5H); 1.87 (s, 6H).

Scheme 3. Preparation of chromophore **V**.

organometallic chromophore **V** in 68% yield. This compound has spectral data consistent with the assigned structure².

3. Conclusions

In summary, two new organometallic π -conjugated push–pull chromophores were prepared. Their original design combine an organometallic donor group, the ferrocene, associated with an aromatic spacer, containing thiophene or 3,3'-bipyridine, and a tricyanofuran or a benzonitrile acceptor. This last acceptor group could be used in the future as a ligand to introduce a second organometallic entity, giving access to bimetallic chromophores.

The synthesis of chromophores **IV** was based on classical organic transformations such as Wittig or Wittig–Horner–Emmons condensations, and Knoevenagel reactions. An alkoxy side chain was introduced

(**IVb**) in order to ultimately incorporate this chromophore covalently in a polymer matrix. The second chromophore, **V**, was obtained via a convergent Suzuki cross-coupling of a 6-(arylvinylyne)-3-bromopyridine derivative and the corresponding pyridinyl boronic ester. These results show that this modular synthetic approach is very attractive in the field of optoelectronics, for example to synthesize other NLO (*i*) organic chromophores bearing more efficient donor/acceptor pairs, and (*ii*) organometallic chromophores to extend the series.

The evaluation of the electrochemical, and linear as well as NLO properties of these new families of organometallic chromophores are under investigation.

References

- [1] H.S. Nalwa, *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, Boca Raton, FL, 1997.
- [2] L. Dalton, in: K.-S. Lee (Ed.), *Advances in polymer Science*, vol. 158, 2001, p. 1.
- [3] J.L. Oudar, D.S. Chemla, *J. Chem. Phys.* 66 (1977) 2664.
- [4] S.R. Marder, L.T. Cheng, B.G. Tiemann, A.C. Friedly, M. Blanchard-Desce, J.W. Perry, J. Skindho, *Science* 263 (1994) 511.

² ¹H NMR (200 MHz, (CD₃)₂CO) δ (ppm): 8.84 (m, 1H); 8.78 (m, 1H); 7.97–7.90 (m, 5H); 7.83–7.69 (m, 4H); 7.10 (d, 1H, $J = 15.4$ Hz); 4.67 (m, 2H); 4.38 (m, 2H); 4.17 (s, 5H); 2.60 (s, 3H); 2.48 (s, 3H).

- [5] (a) M. He, T.M. Leslie, J.A. Sinicropi, *Chem. Mater.* 14 (2002) 2393; (b) M. He, T.M. Leslie, J.A. Sinicropi, *Chem. Mater.* 14 (2002) 4662; (c) M. He, T.M. Leslie, J.A. Sinicropi, S.M. Garner, L.D. Reed, *Chem. Mater.* 14 (2002) 4669.
- [6] C. Zhang, C. Wang, L.R. Dalton, H. Zhang, W.H. Steier, *Macromolecules* 34 (2001) 253.
- [7] (a) Y. Shi, C. Zhang, H. Zhang, J.H. Bechtel, L.R. Dalton, B.H. Robinson, W.H. Steier, *Science* 288 (2000) 119; (b) C. Zhang, L.R. Dalton, M.-C. Oh, H. Zhang, W.H. Steier, *Chem. Mater.* 13 (2001) 3043.
- [8] (a) N.J. Long, *Angew. Chem. Int. Ed.* 34 (1995) 21; (b) H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* (2000) 229; (c) E. Goovaerts; W.E. Wenseleers, M.H. Garcia, G.H. Gross, in: H.S. Nalwa (Ed.), *Handbook of Advanced Electronic and Photonic Materials and Devices*, vol. 9, Non-Linear Optical Materials, Academic Press, New York, 2001, p. 127; (d) P.G. Lacroix, *Eur. J. Inorg. Chem.* (2001) 339; (e) S. Di Bella, *Chem. Soc. Rev.* 30 (2001) 355.
- [9] (a) M.L.H. Green, S.R. Marder, M.E. Thompson, J.A. Bandy, D. Bloor, P.V. Kolinsky, *Nature* 330 (1987) 360; (b) D.R. Kanis, M.A. Ratner, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 10338.
- [10] (a) Z.F. Plyta, D. Prim, J.-P. Tranchier, F. Rose-Munch, É. Rose, *Tetrahedron Lett.* 40 (1999) 6769; (b) J.-P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, Z.F. Plyta, F. Rose-Munch, E. Rose, *Tetrahedron Lett.* 41 (2000) 3607; (c) J.-P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, J.G. Planas, F. Rose-Munch, É. Rose, G.R. Stephenson, *Tetrahedron Lett.* 42 (2001) 3311; (d) M.H. Garcia, S. Royer, M.P. Robalo, A.R. Dias, J.-P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, F. Rose-Munch, É. Rose, J. Vaissermann, A. Persoons, I. Asselberghs, *Eur. J. Inorg. Chem.* (2003) 3895; (e) B. Jacques, J.-P. Tranchier, F. Rose-Munch, É. Rose, G.R. Stephenson, C. Guyard-Duhayon, *Organometallics* 23 (2004) 184; (f) S. Schouteeten, J.-P. Tranchier, F. Rose-Munch, É. Rose, A. Auffrant, G.R. Stephenson, *Organometallics* 23 (2004) 4308.
- [11] (a) A.-J. Attias, C. Cavalli, B. Bloch, N. Guillou, C. Noël, *Chem. Mater.* 11 (1999) 2057; (b) A.-J. Attias, P. Hapiot, V. Wintgens, P. Valat, *Chem. Mater.* 12 (2000) 461; (c) N. Lemaître, A.-J. Attias, I. Ledoux, J. Zyss, *Chem. Mater.* 13 (2001) 1420; (d) Q. Chen, E.H. Sargent, N. Leclerc, A.-J. Attias, *Appl. Phys. Lett.* 82 (2003) 4420; (e) Q. Chen, E.H. Sargent, N. Leclerc, A.-J. Attias, *Appl. Phys. Lett.* 42 (2003) 7235.
- [12] (a) N. Leclerc, I. Serieys, A.-J. Attias, *Tetrahedron Lett.* 44 (2003) 5879; (b) N. Leclerc, L. Galmiche, A.-J. Attias, *Tetrahedron Lett.* 44 (2003) 5883.
- [13] K.R.J. Thomas, J.T. Lin, Y.S. Wen, *J. Organomet. Chem.* 575 (1999) 301.
- [14] J.-X. Zhang, P. Dubbois, R. Jerome, *Synth. Commun.* 26 (1996) 3091.
- [15] G. Koeckelberghs, S. Sioncke, T. Verbiest, A. Persoons, C. Samyn, *Polymers* 44 (2003) 3785.
- [16] A. Skibniewski, G. Bluet, N. Druze, O. Riant, *Synthesis* 3 (1999) 459.