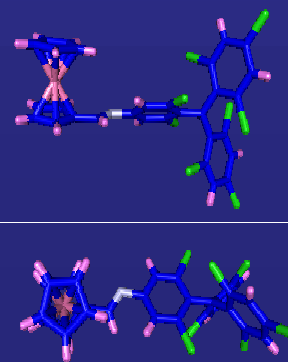


# A New Approach Towards Multiproperty Molecular Materials

Combining Interesting Electric, Magnetic and  
Second-Order Nonlinear Optical Properties

*Ferrocene-Based  
Polychlorotriphenylmethyl  
Radicals*



**Tesi Doctoral**

# **A New Approach Towards Multiproperty Molecular Materials**

**Combining Interesting Electric, Magnetic and  
Second-Order Nonlinear Optical Properties**

***Ferrocene-Based Polychlorotriphenylmethyl Radicals***

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Octubre de 2002**

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CERTIFIQUEN

Que na **Imma Ratera Bastardas**, ha dut a terme sota la seva direcció el treball que porta per títol "*Ferrocene-Based Polychlorotriphenylmethyl Radicals: A New Approach Toward Multiproperty Molecular Materials*" , i que queda recollit en aquesta memòria per a optar al grau de Doctor en Ciència de Materials.

I perquè així consti, signen el present certificat.

Prof. Jaume Veciana i Miró

Dr. Daniel Ruiz Molina

Bellaterra, 1 d'Octubre del 2002

*L'experiència més bonica que tenim al nostre abast és el misteri [...]; la certesa que hi ha quelcom que no podem assolir.*

A. Einstein



*Als meus pares*

El treball que es presenta en aquesta Memòria de Tesi Doctoral ha estat possible gràcies a l'esforç de molta gent a qui tinc moltes coses a agrair. En primer lloc vull expressar el meu agraïment més sincer als dos directors d'aquest treball; el Prof. Jaume Veciana i el Dr. Daniel Ruiz per la seva dedicació constant. Al Prof. Jaume Veciana, per encomanar-me la curiositat científica, sobretot per haver-me obert noves fronteres en el terreny interdisciplinari de la Ciència de Materials, així com també per haver-me donat la possibilitat de mobilitat necessària per respondre a aquesta interdisciplinarietat. Això m'ha permès aprendre a treballar en col·laboració amb altres grups de recerca, així com també conèixer com es fa ciència a altres països i saber comunicar resultats davant altres investigadors. Al Dr. Daniel Ruiz li agraeixo la possibilitat que m'ha donat de ser, d'alguna manera, la seva primera filla científica. Gràcies a ell he pogut tenir un seguiment molt proper de tota la feina. La seva intuïció de pare li ha donat la paciència per escoltar-me, aconsellar-me i sobretot entendre'm en tot moment. Li agraeixo molt l'esforç que ha fet per la realització d'aquesta Tesi, tot el que m'ha ensenyat, així com també la seva proximitat i amistat que l'ha fet ser un director amb qui també hem pogut sortir i passar-nos-ho bé.

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# Contents

## List of Papers 7

### Chapter 1 | Introduction

1.1 Towards Multiproperty Materials.....	11
1.2 Metallocene-based Polychlorotriphenylmethyl Radicals.....	14
1.3 Scope of this Thesis.....	18
References.....	21

### Chapter 2 | Synthesis

2.1 Introduction.....	23
2.2 Synthesis of ferrocene-based monoradicals <b>1-6</b> .....	25
2.2.1 Synthesis of Ferrocenyl Schiff Based Polychlorotriphenylmethyl Radicals <b>3-6</b> .....	25
2.2.2 Synthesis of ( <i>trans</i> )-4-ferrocenylvinylene-2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl) methyl radical <b>1</b> .....	28
2.2.3 Synthesis of ( <i>trans</i> )-4-nonamethylferrocenylvinylene-2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl) methyl radical <b>2</b> .....	30
2.3 Synthesis of ferrocene-based polyradicals <b>7-10</b> .....	33
2.3.1 Synthesis of ( <i>trans-trans</i> )-1,1'-divinylferrocene-bis[2,3,5,6-tetrachloro phenyl-bis(pentachlorophenyl)methyl] diradical <b>7</b> and ( <i>trans-trans</i> )-1,1'-divinylruthenocene-bis[2,3,5,6-tetrachlorophenylbis(pentachlorophenyl)methyl] diradical <b>9</b> .....	33
2.3.2 Synthesis of ( <i>trans-trans</i> )-1,1'-divinylnonamethylferrocene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)methyl] diradical <b>8</b> .....	34
2.3.3 Synthesis of ( <i>trans-trans-trans</i> )-1,3,1'-trivinylruthenocene-tris[(2,3,5,6-tetrachlorophenyl)bis(pentachlorophenyl)] triradical <b>10</b> .....	36
References.....	39

**Chapter 3 | Results**

<b>3.1 Magnetism</b> .....	41
3.1.1 Introduction.....	41
3.1.1.1 Spin Containing Building Blocks.....	42
3.1.1.2 Coupling Routes.....	44
3.1.2 Results.....	47
3.1.2.1 Supramolecular Magnetism.....	48
3.1.2.2 High-Spin Macromolecules.....	58
References.....	62
<b>3.2 Electric Properties</b> .....	65
3.2.1 Introduction.....	65
3.2.1.1 Self-exchange Intramolecular Electron Transfer.....	67
3.2.1.2 Locally Photoinduced Charge Separation.....	71
3.2.2 Results.....	73
3.2.2.1 Optically Induced Self-Exchange Intramolecular Electron Transfer.....	77
3.2.2.2 Locally Photoinduced Intramolecular Electron Transfer.....	84
3.2.2.3 Thermally Induced Self-Exchange Intramolecular Electron Transfer.....	85
References.....	90
<b>3.3 Nonlinear Optical Properties</b> .....	93
3.3.1 Introduction.....	93
3.3.1.1 The Theory of Nonlinear Optics.....	94
3.3.1.2 Experimental Techniques.....	96
3.3.1.3 Materials for Second Order Nonlinear Optics.....	96
3.3.1.4 Open-Shell Systems in NLO.....	100
3.3.2 Results.....	101
3.3.2.1 Octupolar Systems.....	102
3.3.2.2 PTM radicals in Push-Pull systems. <i>Tuning the NLO Response</i> .....	106
References.....	111

**Chapter 4 | Conclusions** 115**New Perspectives** 117

## Chapter 5| Experimental Part

5.1	Instruments and Materials. Solvent and Reagents.....	119
5.2	Synthesis and Characterization.....	120
5.2.1	Synthesis of ( <i>trans</i> )-4-(ferrocenylimino)-2,6-(dichlorophenyl)bis(2,4,6-trichlorophenyl) methyl radical ( <b>3</b> ) and ( <i>cis</i> )-4-(ferrocenylimino)- 2,6-(dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical ( <b>5</b> ).....	120
5.2.2	Synthesis of ( <i>trans</i> )-4-(nonamethylferrocenylimino)-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical ( <b>4</b> ).....	121
5.2.3	Synthesis of bis[pentachlorophenyl]-[4-methyltriphenylphosphonium-2,3,5,6-tetrachlorophenyl] methane bromide ( <b>17</b> ) .....	122
5.2.4	Synthesis of bis[pentachlorophenyl][4-diethylphosphonate-2,3,5,6-tetrachlorophenyl] methane ( <b>20</b> ).....	122
5.2.5	Synthesis of ( <i>trans</i> )-1-ferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl) methane ( <b>18</b> ).....	123
5.2.6	Synthesis of ( <i>trans</i> )-1-ferrocenylvinyl-2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl) methyl radical ( <b>1</b> ).....	123
5.2.7	Synthesis of ( <i>trans-trans</i> )-1,1' ferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl) bis(pentachlorophenyl)] methane ( <b>23</b> ) .....	124
5.2.8	Synthesis of ( <i>trans-trans</i> )-1,1'- ferrocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)methyl] diradical ( <b>7</b> ) .....	125
5.2.9	Synthesis of ( <i>trans</i> )-4-nonamethylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methane ( <b>21</b> ).....	125
5.2.10	Synthesis of ( <i>trans</i> )-4-nonamethylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methyl anion ( <b>22</b> ).....	126
5.2.11	Synthesis of ( <i>trans</i> )-4-nonamethylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methyl radical ( <b>4</b> ).....	127
5.2.12	Synthesis of ( <i>trans-trans</i> )-1,1'-octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl)] methane ( <b>24</b> ).....	127
5.2.13	Synthesis of ( <i>trans-trans</i> )-1,1'-octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl)] methane bisanion ( <b>25</b> ).....	128
5.2.14	Synthesis of ( <i>trans-trans</i> )-1,1' octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl)] methyl diradical ( <b>8</b> ) .....	129
5.2.15	Synthesis of ( <i>trans-trans</i> )-1,1'-ruthenocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methane ( <b>26</b> ) .....	129
5.2.16	Synthesis of ( <i>trans-trans</i> )-1,1'-ruthenocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methyl radical ( <b>9</b> ).....	130
5.2.17	Synthesis of ( <i>trans-trans-trans</i> )-1,3,1'-ruthenocenyldivinylene-tris[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)]methane ( <b>27</b> ) .....	131
5.2.18	Synthesis ( <i>trans-trans-trans</i> )-1,3,1'-ruthenocenyldivinylene-tris[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methyl triradical ( <b>10</b> ) .....	131

5.3	Synthesis and Characterization of Metallocenes.....	132
5.3.1	Synthesis of Dilithioferrocene – TMEDA.....	132
5.3.2	Synthesis of Ferrocenemonoaldehyde (R=H) <b>(29)</b> and Ferrocene-1,1'-dicarbaldehyde (R=CHO) <b>(30)</b> .....	132
5.3.3	Synthesis of 2,3,4,5-Tetramethylcyclopenta-1,3-diene-1-carboxylic acid <b>(31a)</b> and 2,3,4,5-Tetramethylcyclopenta-2,4-diene-1-carboxylic acid <b>(31b)</b> .....	133
5.3.4	Synthesis of 1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-1,3-diene <b>(32a)</b> and 1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-2,4-diene <b>(32b)</b> .....	134
5.3.5	Synthesis of 1,1'-Bis(methoxycarbonyl)-2,2',3,3',4,4',5,5'-octamethylferrocene <b>(33)</b> .....	134
5.3.6	Synthesis of 1,1'-Bis(hydroxymethyl)-2,2',3,3',4,4',5,5'-octamethylferrocene <b>(34)</b> .....	135
5.3.7	Synthesis of 2,2',3,3',4,4',5,5'-Octamethylferrocene-1,1'-dicarbaldehyde <b>(35)</b> .....	135
5.3.8	Synthesis of Cyclopentadiene <b>(36)</b> .....	136
5.3.9	Synthesis of Ruthenocene <b>(37)</b> .....	136
5.3.10	Synthesis of Ruthenocene-1,1'-dicarboxaldehyd (R=H, <b>38</b> ) and Ruthenocene-1,3,1'-tricarbaldehyd (R=CHO, <b>39</b> ).....	136
5.3.11	Synthesis of 1,1',2,2',3,3',4,4'-octamethylferrocene <b>(40)</b> .....	137
5.3.12	Synthesis of Formyl-1',2,2',3,3',4,4',5-octamethylferrocene <b>(41)</b> .....	137
5.3.13	Synthesis of 1-hydroxymethyl-1',2,2',3,3',4,4',5-octamethylferrocene <b>(42)</b> .....	138
5.3.14	Synthesis of 1,1',2,2',3,3',4,4',5-nonamethylferrocene <b>(43)</b> .....	138
5.3.15	Synthesis of Formyl-1',2,2',3,3',4,4',5,5'-nonamethylferrocene <b>(44)</b> .....	139
	References.....	140

## Chapter 6| Crystallographic Data

6.1	Crystallographic Data of Radical 1.....	141
6.1.1	Crystallographic data for radical 1.....	143
6.1.2	Atomic coordinates (Å and equivalent isotropic displacement parameters (pm <sup>2</sup> ) for 1.....	144
6.1.3	Bond distances (Angstroms) of radical 1.....	145
6.1.4	Bond angles (degrees) of radical 1.....	146
6.2	Crystallographic Data of Radical 2 .....	147
6.2.1	Crystallographic data for radical 2.....	149
6.2.2	Atomic coordinates (Å and equivalent isotropic displacement parameters (pm <sup>2</sup> ) for 1.....	149
6.2.3	Bond distances (Angstroms) for radical 2.....	150
6.2.4	Bond angles (degrees) for radical 2 .....	151
6.3	Crystallographic Data of Radical 3.....	153
6.3.1	Crystallographic data for radical 3.....	154
6.3.2	Atomic coordinates (Å and equivalent isotropic displacement parameters (pm <sup>2</sup> ) for 3.....	155
6.3.3	Bond distances (Angstroms) of radical 3.....	156

6.3.4	Bond angles (degrees) of radical 3.....	156
6.4	Crystallographic Data of 18.....	157
6.4.1	Crystallographic Data of 18.....	159
6.4.2	Atomic coordinates (Å and equivalent isotropic displacement parameters (pm <sup>2</sup> ) for 2.....	159
6.4.3	Bond distances (Angstroms) of 18.....	160
6.4.4	Bond angles (degrees) of 18.....	161
6.5	Crystallographic Data of 21.....	163
6.5.1	Crystallographic Data for 21.....	164
6.5.2	Atomic coordinates (Å and equivalent isotropic displacement parameters (pm <sup>2</sup> ) for 21...	165
6.5.3	Bond distances (Angstroms) of 21.....	166
6.5.4	Bond angles (degrees) of 21.....	167

## Chapter 7 | Appendixes

7.1	Time Resolved Absorption Measurements.....	171
7.2	Mössbauer Spectroscopy.....	175
7.2.1	Introduction.....	175
7.2.2	Nuclear Physics of Fe <sup>57</sup> .....	176
7.2.3	Hyperfine Interactions.....	176
7.2.3.1	Isomer Shift.....	176
7.2.3.2	Electric Quadrupole Interaction.....	177
7.2.3.3	Magnetic Hyperfine Interaction.....	177
7.2.4	Experimental Set-up.....	177
7.2.4.1	Mössbauer Spectroscopy of the laboratory of the University of Mainz .....	178
References.....		180
7.3	Nonlinear Optical Measurements.....	181
7.3.1	Introduction.....	181
7.3.2	Hyper-Rayleigh Scattering Technique.....	181
7.3.2.1	Molecules Without Dipole Moment: Octupoles.....	184
7.3.2.2	Experimental Aspects of Hyper-Rayleigh Scattering in Solution.....	184
7.3.2.3	Laboratory and Molecular Reference Frame.....	186
7.3.3	Electric Field Induced Second Harmonic Generation Technique.....	187
7.3.3.1	“Phase Matching”.....	187
7.3.3.2	Light Source.....	188
7.3.3.3	Nonlinear Optical Spectrometer.....	189
7.3.3.4	Experimental Problems in $\beta$ Determination.....	191
References.....		192

## Chapter 8 | Publications

Papers Revised by the Doctoral Commission

Papers After the Doctoral Commission

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# List of papers

This thesis is referred to the following papers, which will be cited in the text by their roman number

## Papers revised by the Doctoral Commission:

- I. **A new Photomagnetic Molecular System Based on Photoinduced Self-Assembly of Radicals**  
I.Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, K. Wurst, Nathalie Daro, J.-F. Létard, C. Rovira, J. Veciana  
  
*Angew. Chem. Int. Ed. Engl.* **2001**, *40*, No.5, 919
  
- II. **Formation of a Biradical Species from a Monoradical with a Photoisomerizable Imine Group**  
D. Ruiz-Molina, I. Ratera, J. Vidal-Gancedo, N. Daro, J.-F. Létard, C. Rovira, J. Veciana  
  
*Synthetic Metals*, **2001**, *121*, 1804.
  
- III. **EPR Study of the *cis* and *trans* Isomers of a Ferrocenyl Schiff-Base Polychlorotriphenylmethyl Radical**  
I.Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, C. Rovira, J. Veciana,  
  
*Polyhedron*, **2001**, *20* (11-14) 1643-1645.
  
- IV. **Ferrocene as a Ferromagnetic Coupler. Synthesis and Characterization of a Ferrocene Bridged Polychlorotriphenylmethyl Diradical**  
O. Elsner, D. Ruiz-Molina, I. Ratera, J. Vidal-Gancedo, C. Rovira, J. Veciana,  
  
*J. Organomet. Chem.*, **2001**, (637-639), 252-257
  
- V. **Nonlinear Optical Properties of a New Stable Ferrocenyl Schiff-base Polychlorotriphenylmethyl Radical**  
I.Ratera, D. Ruiz-Molina, C. Sánchez, R. Alcalá, C. Rovira, J. Veciana, ,  
  
*Synthetic Metals*, **2001**, *121*, 1834.

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**Papers after the Doctoral Commission:**

- VI. Non Linear Optical properties of Polychlorotriphenylmethyl Radicals. Towards the Design of “Super-Octupolar” Molecules**  
I.Ratera, J.-F. Létard, S. Marcén, D. Ruiz-Molina, E. Freysz, C. Rovira, J. Veciana

*Chem. Phys. Lett.*, **2002**, 363, 245-251

- VII. Intramolecular Electron Transfer in Organic Molecules. Molecular Nanowires.**

D. Ruiz-Molina, J. Vidal-Gancedo, J. Sedó, I. Ratera, J. Veciana and C. Rovira  
*Molecular Low Dimensional and Nanostructured Materials for Advanced Applications (MMAA)*, p.125-138. Edited by A. Graja, B. R. Bulka and F. Kajzar.  
*NATO ASI Series, II. Mathematic, Physics and Chemistry, ISBN 1-4020-0578-4, Vol. 59, 2002*

- VIII. Nonlinear Optical Properties of Open-Shell Polychlorotriphenylmethyl Radicals**

I.Ratera, D. Ruiz-Molina, C. Sporer, S. Marcen, S. Montant, J.-F. Létard, E. Freysz, C. Rovira, J. Veciana

*Polyhedron*, (In press)

- IX. A new Valence Tautomerism Example in an Electroactive Ferrocene Substituted Triphenylmethyl Radical**

I.Ratera, D. Ruiz-Molina, F. Renz, J. Ensling, K. Wurst, C. Rovira, P. Gütllich, J. Veciana..

*J. Am. Chem. Soc.* (In press)

- X. Supramolecular Photomagnetic Materials: Photoinduced Self-Assembly of Ferrocene-Based Polychlorotriphenylmethyl Radicals**

I.Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, C. Rovira, J. Novoa, K. Wurst, C. Rovira, J. Veciana

*Chem. Eur. J.* (submitted)



**Manuscripts in Preparation (not included):**

- XI. Synthesis and Characterization of Ruthenocene-Based Polychlorotriphenylmethyl Diradical and Triradical Compounds**  
I.Ratera, D. Ruiz-Molina, C. Sporer, J. Vidal-Gancedo, C. Rovira, J. Veciana,.
- XII. Ferrocene-Based Polychlorotriphenylmethyl Radical: A Multifunctional Molecular Switch**  
C. Sporer, I. Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, C. Rovira, J. Veciana,.
- XIII. Intramolecular Electron Transfer Phenomenon in Ferrocene based Polychlorotriphenylmethyl Radicals: Solvent Effects and Photophysical Properties**  
I.Ratera, D. Ruiz-Molina, J. Baggerman, A-M. Brouwer, C. Rovira, J. Veciana.
- XIV. Nonlinear Optical Properties of Open-Shell Ferrocene-based-Polychlorotriphenylmethyl Radicals**  
I.Ratera, D. Ruiz-Molina, C. Sporer, S. Marcen, S. Montant, J.-F. Létard, E. Freysz, C. Rovira, J. Veciana.



# 1 | Introduction

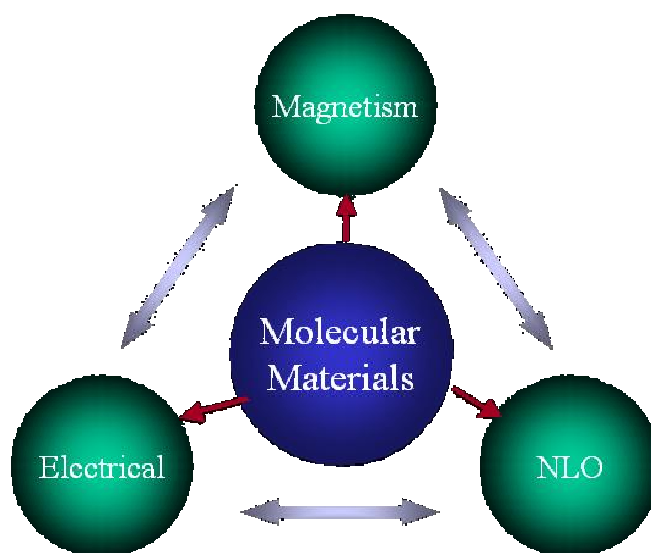
## 1.1 TOWARDS MOLECULAR MULTIPROPERTY MATERIALS

In the last years there is much interest in the field of Molecular Materials (MM).<sup>1,2,3</sup> The interest arises from their expectations in future emerging technologies as well as to improve those already existing nowadays.<sup>4,5,6</sup> MM are constituted by purely organic or metal-organic building blocks that can be obtained by typical synthetic methods. Once obtained, they are organized in a condensed phase (either crystalline material, liquid crystal, thin film, etc...) showing interesting conducting,<sup>7,8</sup> optical<sup>9,10</sup> or magnetic properties.<sup>11</sup> MM are also easy-handle and procurable materials whose properties may be fine-tuned at will through chemical synthesis previous molecular design? Indeed, traditional inorganic materials are usually submitted to very high temperatures during the synthetic process, which ensures thermodynamic stability, but leads to limited chemical flexibility. By contrast, molecular materials are obtained in two steps, the first step being the design of a series of “building blocks” and the second being their engineering in various solid-state environments. In this order, there are hundreds of chemical modifications that can be envisioned for a molecular unit by means of organic synthesis or coordination chemistry methods. This fact allows modulation of the interaction between the blocks and, hence, nearly identical molecular units can lead to different bulk properties. In addition to the properties previously mentioned, other advantages of MM are their considerable reduced weight, versatility and transparency between others. Even though the enormous interest for MM, there are also considerable limitations that should be worked out in a near future to improve their performance. For instance, the relative stability of some of these materials or the enormous difficulties found to control and/or predict their supramolecular arrangement within a crystalline network. The improvement of such limitations has become the main objective of several scientific groups working in the field of MM around the world. Another driving force for people working in the topic of MM has become the development of *Multiproperty Molecular Materials*.<sup>12,13,14</sup>

### *Multiproperty Molecular Materials*

The versatility of molecular chemistry offers a unique opportunity to meet additional challenges, such as designing multiproperty materials that would simultaneously possess several properties<sup>15</sup> (magnetism and conductivity, magnetism and non-linear optical (NLO) properties<sup>16,17</sup> or conductivity and NLO properties<sup>18,19,20</sup>). The presence of two cooperative

properties in the same crystal lattice might result in new physical phenomena and novel applications that are difficult or impossible to combine in a conventional inorganic solid with a continuous lattice. Such unusual properties may attract some interest in multidisciplinary technologies where several properties need to be linked in the same device, like optoelectronics technologies, which integrates photonic devices with standard semiconductor electronics.



**Figure 1.** Interplay between the different properties shown by Molecular Materials

One of the approaches most successfully used for creating this type of multifunctional (multiproperty) materials is the formation of hybrid organic/inorganic crystals comprising two functional sub-lattices exhibiting distinct properties. Following this approach, Coronado et al. recently reported the coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound made of bimetallic oxalate magnetic layers and conducting BEDT-TTF cations.<sup>21,22</sup> In this material, the conducting electrons in the organic layer do not appear to interact with the magnetic moments of the ferromagnetic layer in contrast with inorganic systems where the mobile electrons play a crucial role either on the magnetic interactions or the conductivity. This unique feature, which is only possible because of the molecular nature of the system, may yet yield unforeseen physical characteristics although it will be also desirable to develop hybrid molecular materials in which the conducting and magnetic subsystems do interact with each other. Such interaction would be crucial to the development, for instance, of new magneto-resistant systems.

The formation of hybrid organic/inorganic crystals comprising two functional sub-lattices has also been found of particular interest to obtain organic NLO chromophores embedded in an inorganic magnetic matrix. The advantages of this approach are twofold. First, the inclusion of chromophores into organic and inorganic hosts has been used to permanent stabilizing the polar order of chromophores (non-Centro symmetric order) generating an observable bulk hyperpolarizability effect. The second reason arises from the

nanocomposite nature of the material, for which the superposition of the properties of the guest and the magnetic host lattice is expected to appear. For instance, Clement et al. have provided a set of layered compounds comprising a series of bimetallic oxalate complexes with five different metals (M=Mn, Fe, Co, Ni, Cu) and seven stilbazolium-shaped organic dyes. Although all these hybrid structures order ferromagnetically at Curie temperatures in the 6-13 K range and exhibit high SHG efficiencies, both components are fairly well separated with no effect of the magnetization on the NLO response ( $\beta$ ). However, a deeper theoretical level predicts that the usual NLO framework could be enlarged to encompass both electric and magnetic dipole transitions, leading to generalized mixed electric-magnetic contributions to NLO tensors.<sup>16, 17</sup>

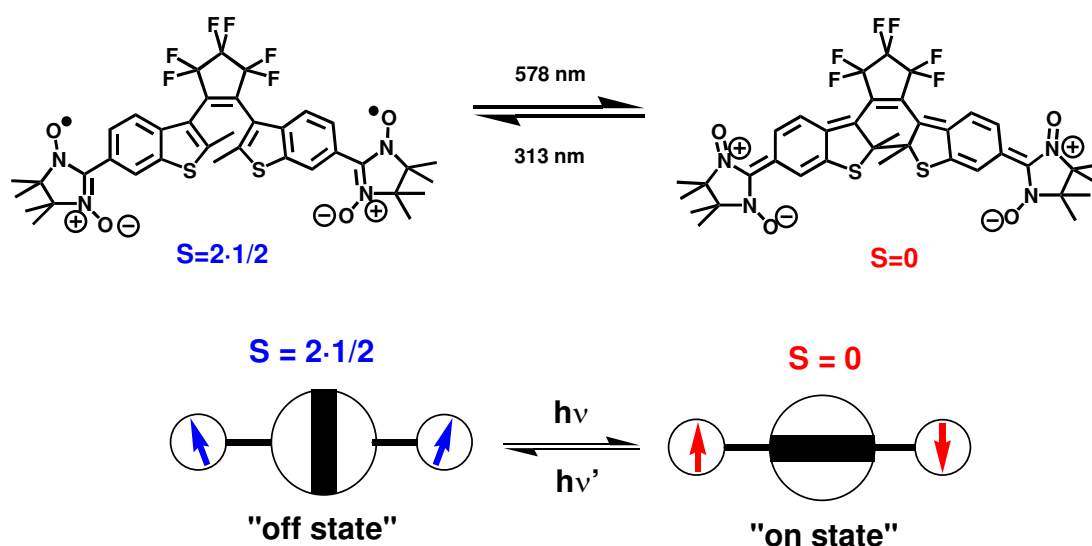
Up to now examples combining magnetism and conductivity as well as magnetism and nonlinear optical (NLO) properties have been described. By contrast, the investigation of the interface between conducting and NLO properties is rather a new topic. Linking conductivity and NLO properties at a molecular level is a challenging target, even if the possibility of using such materials in an operating electro-optical device may still remain somewhat speculative. At first, it seems possible to link NLO and conductivity in a molecular salts as both properties deal with the same general concept: an intermolecular charge transfer along stacks of ions in conducting systems and an intramolecular charge transfer between a donor (D) and an acceptor (A) counterpart. Following this approach, Lacroix et al. have recently reported on a strategy aimed at combining conducting inorganic layers built up from nickel bis(dithiolene)metal complexes and various highly polar cyanine dyes.<sup>23</sup>

All the examples of multiproperty molecular materials combining NLO and/or magnetic and/or electrical properties previously described are based on the formation of hybrid organic/inorganic sub-lattices comprising distinct properties. On the contrary, examples of multiproperty molecular materials with different properties coming all from the same molecular building block are scarce. If realizable, such systems will promote a stronger synergistic effect between the different properties studied. For instance, the discovery of new molecular NLO materials having open-shell electronic structures is in its early stage even though open-shell electronic species can exhibit very large second-order hyperpolarizabilities in comparison with analogous closed-shell systems. Up to now only a few examples of metal-organic transition metal complexes showing open-shell character and second-order hyperpolarizabilities have been described.<sup>24,25</sup> Finally, if the combination of magnetism and NLO properties or conductivity and NLO properties within the same molecular building block results complicated, even more difficult is the obtaining of molecular materials with coexisting ferromagnetism and conductivity due to the incompatibility of mobile electrons for both type of properties.

Therefore, before any practical application for multiproperty molecular materials is to be achieved, new systematic studies of simple models that allow us to obtain rules for the prediction and control of the synergism between different properties in multiproperty systems are highly required. If such studies are convenient, not less important results the search for switchable multiproperty molecular materials.<sup>26,27</sup>

## Molecular Switches

The intriguing concept of molecular switches has recently attracted great interest from a variety of perspectives.<sup>28</sup> A molecular-scale switch is a fundamental component of any true molecular electronic/photonics device. An equally important, but more immediately realisable objective is the production of materials, which exhibit useful bulk electronic/magnetic/photonics properties that can be switched by stimulating changes at the molecular and/or macroscopic levels.<sup>29,30</sup> To achieve a pronounced switching effect, the molecule must be stable in two (or more) states that exhibit very different properties and that interconvert reversibly in response to different external stimuli such as temperature, pressure or irradiation.<sup>31,32,33</sup> Complete reversibility and a high speed of switching are also highly desirable for practical applications. A nice example of a molecular was described by Matsuda and co-workers, who successfully design a diradical species that can cross over from a triplet state to a singlet state by using the intervening photochromic coupling unit (Figure 2).<sup>34</sup>

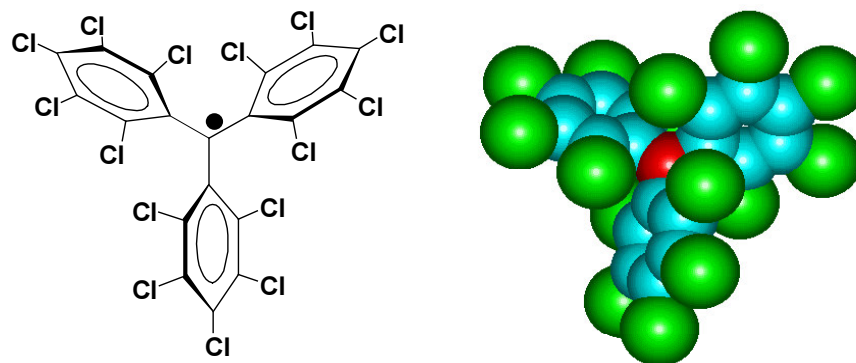


**Figure 2.** Example of an organic photochromic spin crossover system whose magnetic properties are tuned at will by an external stimulus (UV-Visible light).

## 1.2 METALLOCENE-BASED POLYCHLOROTRIPHENYLMETHYL RADICALS

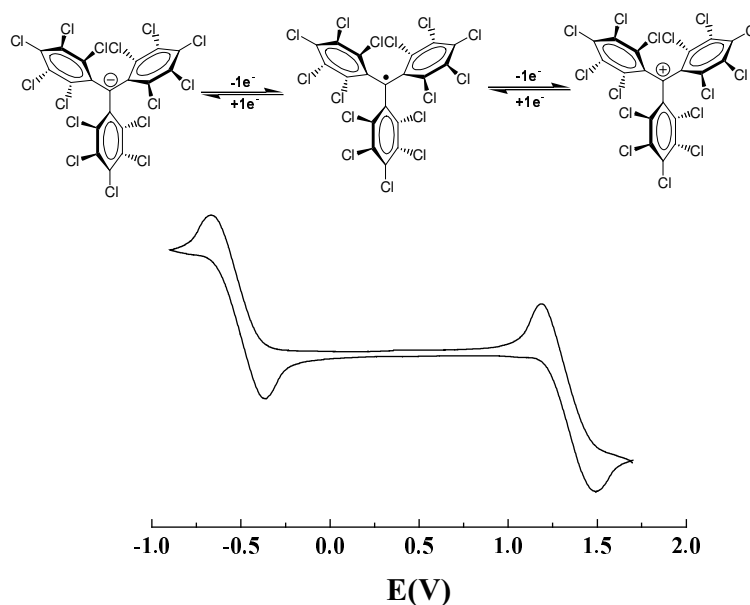
In our group, as part of a general effort aimed at extending the range of multiproperty molecular materials and within the framework of this Thesis, we have centred our attention in the exploration of the unusual properties of ferrocene-based polychlorotriphenylmethyl radicals. Where does the interest for this type of compounds come from? Ferrocene-based polychlorotriphenylmethyl radicals are expected to combine two or more of such properties without the need to combine an additional organic or inorganic matrix, as detailed hereby:

1) Polychlorinated triphenylmethyl (PTM) radicals are open-shell organic units with a net magnetic moment and high thermal and chemical stabilities.<sup>35,36</sup> Indeed, PTM radicals have all their open-shell centres (or trivalent carbon atoms) sterically shielded by an encapsulation with six bulky chlorine atoms in order to increase their life expectancies and thermal and chemical stabilities. For instance, it is very well known that the monoradical counterpart, the perchlorotriphenyl methyl radical shows an astonishing thermal and chemical stability for which the term of inert free radical was coined.<sup>37</sup>



**Figure 3.** Representation of the perchlorotriphenylmethyl radical unit showing the high steric shielding of the central carbon atom surrounded by six bulky chlorine atoms located at the *ortho* positions.

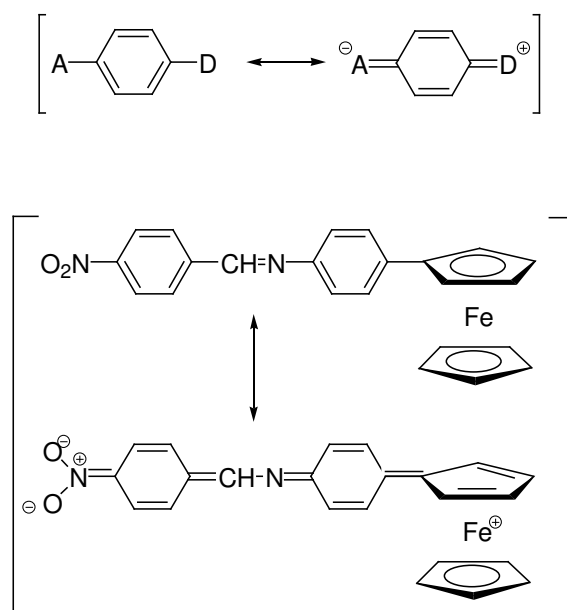
The high persistence as well as the particular structural and conformational characteristics of these radicals has permitted, prior to this thesis, not only to functionalise them to obtain transition metal complexes but also to build pure organic open-shell dendrimers with high-spin ground states and low-spin excited states inaccessible even at room temperature.<sup>38,39,40</sup>



**Figure 4.** Cyclic voltammogram of the perchlorotriphenylmethyl radical showing the formation of the corresponding anionic and cationic forms.

Moreover, such radicals are also interesting because they are electroactive species. Indeed, as shown in Figure 4, the cyclic voltammetry of perchlorotriphenylmethyl radical exhibits two different stable ionic species that correspond to the oxidation and reduction of this radical, giving rise either chemically or electrochemically to the corresponding anions and cations, which are also quite stable species both in solution and in solid state.<sup>41</sup> Nevertheless, reduction of these radicals turns out to be more feasible than the corresponding oxidation, fact that makes this type of radicals as excellent acceptors units to be used as building blocks in NLO systems and/or to achieve intramolecular electron transfer in molecular wires.

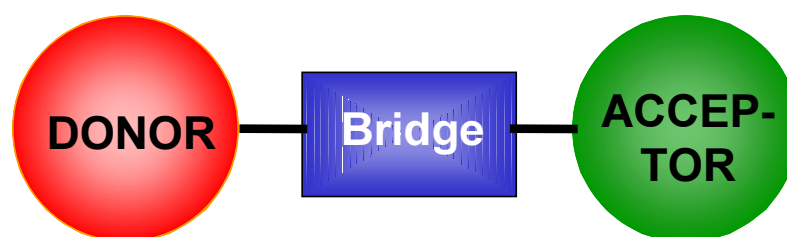
2) Metallocenes are excellent candidates to construct building blocks for *Multiproperty Molecular Materials*. Metallocene units not only exhibit a rich chemistry and synthetic availability but they are also electroactive species whose oxidation state can be controlled by means of a chemical or electrochemical stimulus having moreover their oxidized states an open-shell character.<sup>42</sup> Another advantages of using metallocene units are: a) metallocene systems can possess metal-to-ligand or ligand-to-metal charge transfer bands in the visible region of the spectrum that are usually associated with large second-order NLO activity; b) compounds containing metallocene units have great possibilities for redox changes, a property largely associated with the metal centre, which can be electron-poor or electron-rich depending on the oxidation state and ligand environment. This fact, together with the rich electroactivity of PTM radicals, make this type of systems excellent candidates to construct electrochemical molecular switching devices and c) many organometallic compounds have low-energy excited states with excited-state dipole moments significantly different from their respective ground-state dipole moments. Most of these excited states involve transfer of electron density that will provide a substantial contribution to the NLO response ( $\beta$ ) (see Figure 5).<sup>43</sup>



**Figure 5.** Ground state and lowest energy excited state structures for a conjugated aromatic system.



3) The combination of PTM radicals and metallocene units through covalent bonds will yield Donor-Acceptors molecular systems for which the combination of interesting magnetic, optical and electrical properties are expected. For instance, the synergism of the ferrocene unit acting as a donor group and the PTM radical acting as an acceptor group is expected to promote interesting NLO responses. Correlated with the presence of NLO properties, the presence of intramolecular electron transfer phenomena from the ferrocene to the radical unit is also expected to take place. Moreover, the open-shell character of the organic unit will favour the presence of magnetic ground states.



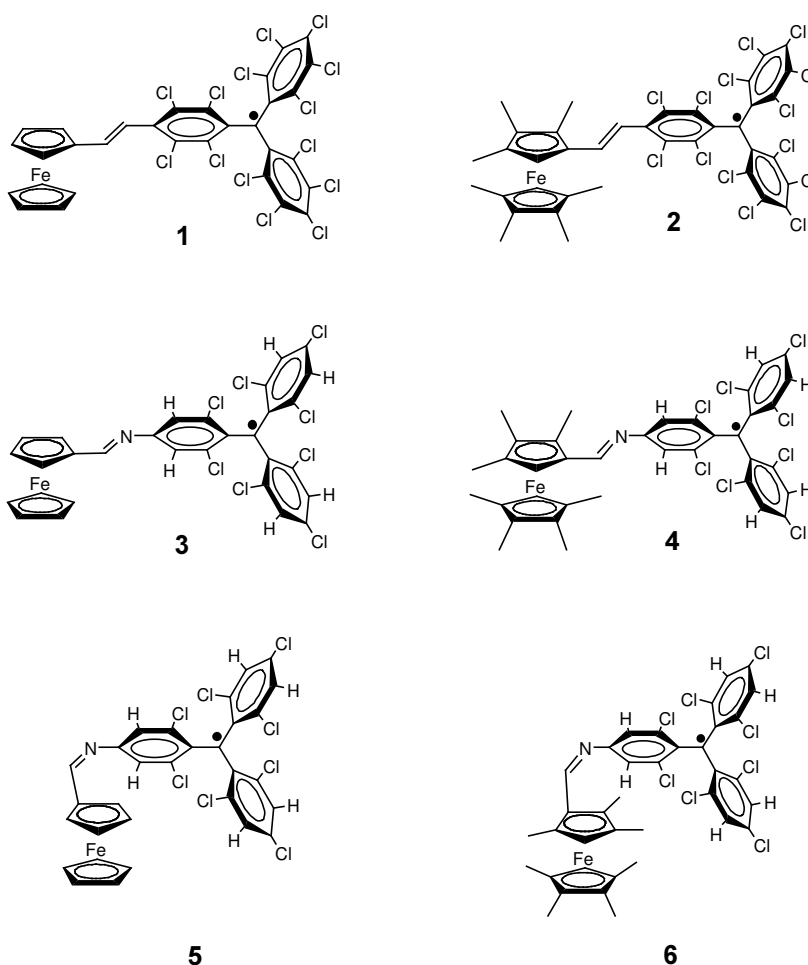
**Figure 6.** Schematic representation of typical Donor-bridge-Acceptor system showing NLO properties

Finally, it has to be remarked that ferrocene-based radicals may also have remarkable implications within the emerging world of Nanotechnology, most precisely *Molecular Electronics*. The purpose of Molecular Electronics is to demonstrate the integration of molecules into scalable, functional electronic devices that are connected to each other and to the outside world in a realistic and practical manner. In other words, the desire for molecular electronics is to use molecules to achieve further miniaturization, greater functionality, and faster clock rates for advanced electronic systems that operate under a wide range of temperatures. Moreover, it may take advantage of three-dimensional structures directed by self-assembly techniques.<sup>44,45</sup> The long-term goal is to provide moderate computational power and high-density memory in an extremely small, low-power format, which will not require multibillion-dollar facilities of complementary metal-oxide semiconductor (CMOS)-based integrated circuits. Indeed, the enormous difficulties found in the last few years when constructing next-generation fabrication facilities aimed many researchers to focus their attention in the design and obtaining of new alternatives to CMOS-based computational systems, mainly based on molecular components. For this reason, the feasibility to promote the use of ferrocene-based radicals in molecular scale devices will be also discussed in future chapters.

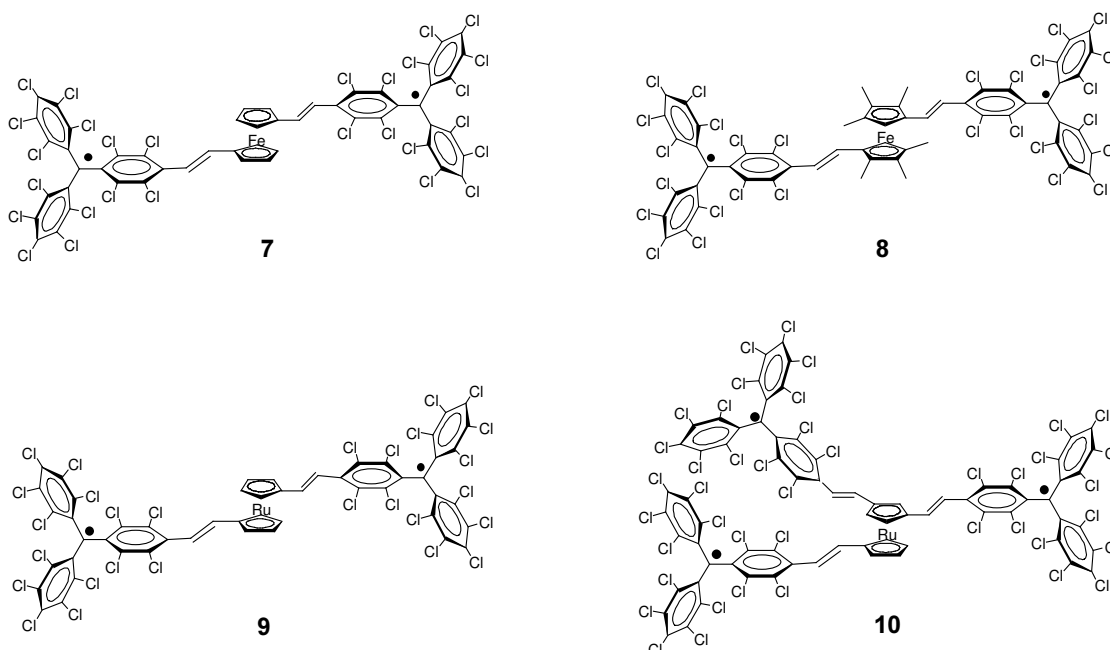
### 1.3 SCOPE OF THIS THESIS

In summary, the main objective of this Thesis is to exploit the techniques of chemistry in the development of the design, synthesis, and physical characterization of different metallocene-based polychlorotriphenylmethyl radicals, which may have specified magnetic, optical and/or electronic multiproperties, including new and interesting phenomena such as bistability which may have important implications in molecular-scale electronic devices. More expressly:

1. Synthesis and chemical characterization of the series of ferrocene-based polychlorotriphenylmethyl monoradicals **1-6** shown below. One of the main advantages of such donor-bridge-acceptor systems is the possibility to tune their properties by changing the donor ability of the ferrocene unit, the acceptor ability of the radical unit and the nature of the  $\pi$ -bridge. The donor ability of the ferrocene unit is modified by including methyl groups. The acceptor ability of the radical unit is modified by varying the number (3 or 5) of electron withdrawing chlorine atoms onto the phenyl rings. And finally, two different types of  $\pi$ -conjugated bridges have been used, an imino and an ethylene group.



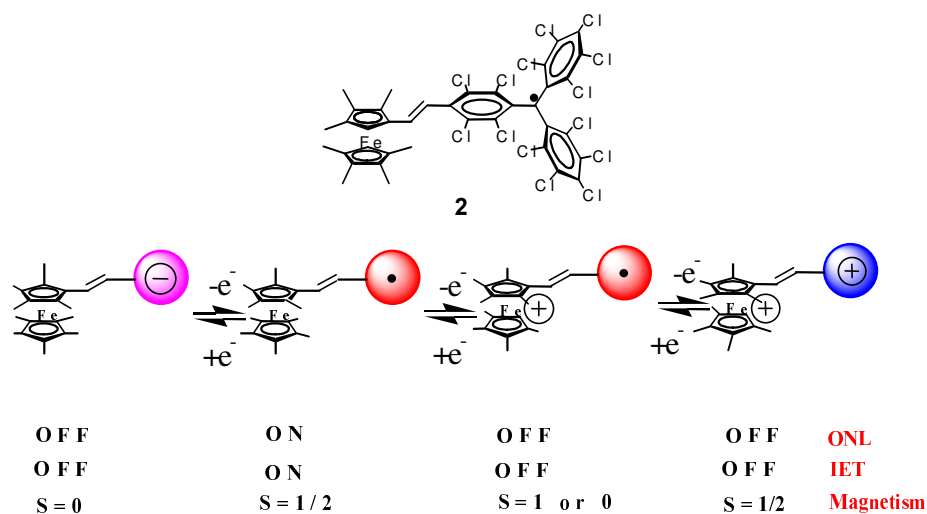
2. Study of the magnetic, electrical and NLO properties of radicals **1-6**. The magnetic properties of these radicals will be studied in solution and in solid state by different techniques including a SQUID magnetometer and Electron Paramagnetic Resonance (EPR). The electronic properties, including the possible presence of Intramolecular Electron Transfer (IET) phenomena, will be studied by different spectro-electrochemical techniques and, when required, by picosecond time resolved transient absorption. And finally, NLO properties will be studied by EFISHG and Hyper-Raleigh Scattering techniques.
3. Synthesis and chemical characterization of the series of ferrocene-based polychlorotriphenylmethyl polyradicals **7-10** shown below. The objective to obtain such polyradicals was twofold. The first objective was to check if the presence of two or more radicals with one ferrocene promotes the presence of synergistic effect that enhances the magnetic, electrical or NLO properties of this family of radicals. The second objective was to study the capability of metallocene bridges as new organometallic magnetic couplers to transmit magnetic interactions between polychlorotriphenylmethyl radicals.



4. Study of the magnetic, electrical and NLO properties of radicals **1-6**. The magnetic properties of these radicals will be studied in solution and in solid state by different techniques including a SQUID magnetometer and Electron Paramagnetic Resonance (EPR). The electronic properties, including the possible presence of Intramolecular Electron Transfer (IET) phenomena, will be studied by different spectro-electrochemical techniques and, when required, by picosecond time resolved

transient absorption. And finally, NLO properties will be studied by EFISHG and Hyper-Raleigh Scattering techniques.

5. The last of the objectives for the present Thesis is the development of molecular switching mechanisms that allow the control of either the magnetic, electrical and optical properties of ferrocene-based polychlorotriphenylmethyl radicals. With this aim, two main strategies have been explored: I) development of a photochemical switch based upon the structural changes promoted by an external irradiation and II) development of an electrochemical multistate switch, like the one shown below.



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