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Ferrocene as a ferromagnetic coupler. Synthesis and characterization of a ferrocene bridged polychlorotriphenylmethyl diradical

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Abstract

A polychlorotriphenylmethyl diradical connected by a 1,1′-ferrocenylendivinylene bridge has been synthesized and characterized. ESR frozen solution experiments down to helium temperature showed that the organometallic unit acts as a ferromagnetic coupler. This fact was supported by ZINDO/1 semiempirical calculations, which showed that the two singly occupied molecular orbitals (SOMOs) are non disjoint in addition to be almost degenerated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferromagnetism; Organic radical; Ferrocene; ESR

1. Introduction

The synthesis and characterization of high-spin macromolecules with purely organic spin-carrier centers have attracted great interest [1]. One of the basic tools to realize such high-spin macromolecules is the *m*-phenylene bridge since it acts as a ferromagnetic coupler when it connects two open-shell units. Indeed, since the Schlenk hydrocarbon, first prepared in 1915 [2], high-spin alignment in the ground state has been successfully demonstrated for several 1,3-phenylene connected carbenes [3] and radicals based on triarylmethyl [4], nitrogen-centered [5] and aminoxyl units [6]. Efforts to increase the number of the aligned spins using 1,3-phenylene couplers have been disturbed by the presence of spin defects and/or bond distortions, which have been shown to affect the ferromagnetic exchange coupling through *m*-phenylenes [7]. To overcome such problems, other complementary approaches such as the use of π-conjugated linear polymers bearing pendant radical groups [8], π-conjugated polycyclic polymers with alternative coupling pathways [9], or the use of diamagnetic metal ions as ferromagnetic couplers [10], have been used. Indeed, in the case of π-conjugated linear polymers bearing pendant radical groups, the radical units are π-conjugated with the backbone so ferromagnetic interactions take place. The main advantage of these polyradicals is that in spite of the great number of spins accumulated along the polymeric backbone, the ferromagnetic interaction is not sensitive to the spin defects that are unavoidable for macromolecular polyradicals. The main drawback is the weakness of the ferromagnetic interactions obtained with this approach. π-Conjugated polycyclic polymers have also been shown to minimize the interruption of the exchange coupling. Following this approach, a macrocyclic polyradical with an average $S = 10$ below 5 K has been reported [9]. Alternatively, when diamagnetic metal ions are coordinated by radical ligands, those may be assembled so that ferromagnetic spin alignments are obtained. For instance, superexchange through orthogonal magnetic orbitals has been observed in a gadolinium complex octahedrally coordinated by three semiquinone radicals [10].

In our group, we focussed our attention in the development and study of new coupling units able to promote ferromagnetic interactions between pure organic radicals. Metallocenes were excellent candidates to be prospected as magnetic couplers not only because of their rich chemistry but also because they are electroac-

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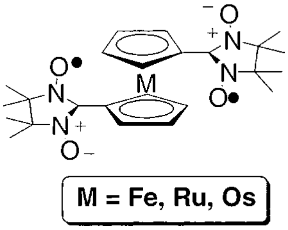


Chart 1.

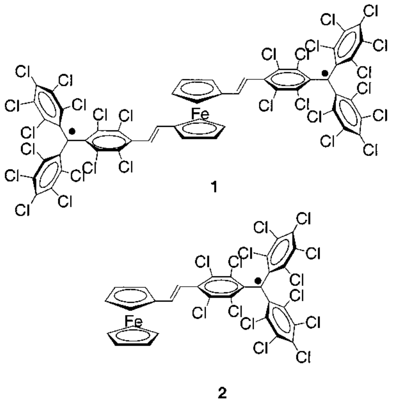
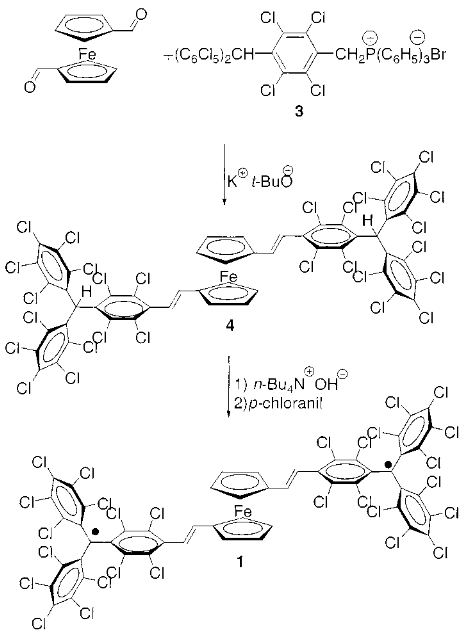


Chart 2.

tive species whose oxidation state can be controlled by means of a chemical or electrochemical stimulus having moreover their oxidized states an open-shell character. However, although metallocenes have been successfully used as building blocks of molecular solids promoting intermolecular magnetic exchange interactions [11], their use as intramolecular magnetic couplers was not studied. Recently, we reported a novel family of compounds consisting of two purely organic α-nitronyl aminoxyl radicals connected by different 1,1′-metallocenylene bridges (see Chart 1). In these compounds, the metallocene units were shown to act as effective magnetic couplers that transmit the magnetic interactions through their skeletons [12]. Nevertheless, the small spin density located on the metallocene units of these systems and the presence of intramolecular hydrogen bonds, which determines the existence of a direct intramolecular through-space magnetic interaction, lead to the appearance of an effective antiferromagnetic interaction between the two α-nitronyl aminoxyl radical units that is very sensitive to the molecular conformation [13]. For this reason, such complexes were not suitable candidates to study and rationalize the behavior of 1,1′-metallocenylene bridges as magnetic couplers.

In order to overcome both inconvenients, diradical **1** consisting of two polychlorinated triphenylmethyl radicals connected by a 1,1′-ferrocenylendivinylene bridge, was designed [14]. The particular structure and topology of such a diradical allow us to expect a non-negligible spin density on the ferrocene moiety making feasible the magnetic coupling between the two organic radical units. In addition, the location of both radical units far away from each other avoids any possibility of having intramolecular hydrogen bond interactions, and consequently, a significant direct through-space magnetic interaction (Chart 2).



Scheme 1.

2. Results and discussion

2.1. Synthesis of ferrocenyl diradical 1

As outlined in Scheme 1, the synthetic route for preparing diradical **1** is based on two main steps. First, a Wittig reaction between the corresponding ferrocene dicarboxaldehyde derivative and the phosphonium bromide precursor **3** that yields the π-conjugated hydrocarbon **4**. Second, the deprotonation of hydrocarbon **4** and the subsequent oxidation of the resulting dicarbanion to yield the desired diradical **1**.

In the first step of the synthesis of **1**, the {4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzyl}(triphenyl)-phosphonium bromide (**3**) [19] was reacted with ferrocene 1,1′-biscarboxaldehyde to give (*E*,*E*)-1,1′-divinylferrocene-β,β′-ylene-bis-(4-tetradecachlorotriphenylmethane) (**4**). This reaction is strongly stereoselective since it yields exclusively the *E*,*E* isomer as ascertained by IR and ^{1}H-NMR data [15]. Such stereoselectivity is justified if we consider that the ylide derived from the phosphonium bromide is stabilized by the presence of a polychlorinated aromatic ring. In addition, the *Z*/*E* isomer distribution of the Wittig products is also strongly influenced by the nature of the base used in the preparation of the ylide [16]; being the potassium *tert*-butoxide, used in this work, the base of choice for maximizing the yields of *E*-olefins [17]. Finally, a THF solution of **4** was treated with an excess of *n*-$Bu_4N^+OH^-$, and the resulting dianion was oxidized with *p*-chloranil to yield the (*E*,*E*)-1,1′-divinylferrocene-β,β′-ylene-bis-(4-tetradecachlorotriphenylmethyl) diradical (**1**), which was isolated as a clathrate (**1**·$2C_6H_6$) after chromatographic purification and recrystallyzation from C_6H_6. The resulting diradical, which is completely stable in air both in the solid state and in diluted solutions, was obtained as dark green microcrystals that were characterized by elemental analysis, cyclic voltammetry, IR, UV–vis and ESR spectroscopies.

Interestingly, diradical **1** retained the *E*,*E* configuration of its precursor, as ascertained by spectroscopic data, in spite of the use of a strong base and an oxidizing agent [19].

2.2. Electrochemical studies

Electrochemical studies of **1** in CH_2Cl_2, with *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte and using a Pt wire as a working electrode, were done at room temperature. The cyclic voltammetry of diradical **1** (Fig. 1) shows one reversible oxidation process at + 666 mV and one reversible reduction process at − 181 mV (vs. Ag/AgCl), that involves the simultaneous transfer of two electrons.

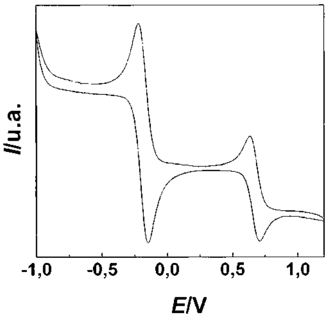


Fig. 1. Cyclic voltammogram, recorded in a CH_2Cl_2 solution containing Bu_4NPF_6 (0.1 M), of diradical **1**.

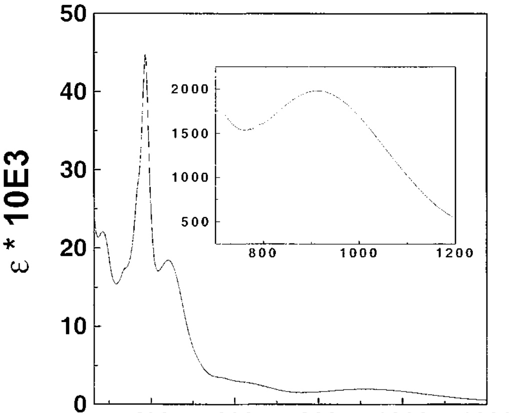


Fig. 2. UV–vis–near IR spectra of diradical **1** in THF.

The oxidation process was assigned to the oxidation of the ferrocene unit, while the reduction process was assigned to the simultaneous reduction of both triphenylmethyl radical units. This result suggests the presence of a very weak or negligible electronic interaction between the triphenylmethyl units since in the case of a strong or moderate electronic interaction between the two units, two electrochemical waves are anticipated. Only if both units exhibit very weak or negligible electronic interactions, the two standard redox potentials must be very close and a single two-electron wave will be observed, with minor differences in shape with respect to a true bielectronic process. The cyclic voltammetric peak separation of the reversible reduction waves (90 mV), which is close to the expected theoretical separation of 59 mV, serves as a criterion to unequivocally assign the electrochemical reversibility of the process. The slightly higher peak separation may arise from the high resistance of the solutions used for the measurements. It is also important to emphasize that the oxidation process of the ferrocene unit of diradical **1** appears at a higher potential value than those observed for the related monoradical species **2** and the unsubstituted ferrocene [14]. This fact is the first direct evidence for the presence of an electronic interaction between the radical and the ferrocene units.

2.3. UV–vis–near IR spectroscopy

Electronic absorption spectra of polychlorotriphenylmethyl radicals usually show an intense absorption band at 386 nm and two weaker bands centered between 565 and 605 nm, all of which are assigned to the radical character of the triphenylmethyl units [18]. The absorption spectra of diradical **1** (Fig. 2) shows an intense absorption at 387 nm ($\varepsilon = 44\,900$) and a weaker band at 442 nm ($\varepsilon = 18\,500$). The band at 442 nm is unprecedented in unsubstituted chlorinated triarylmethyl radicals and can be therefore ascribed to a large electronic delocalization of the unpaired electron into the π-conjugated system. A similar absorption has been recently observed in a *p*-divinylbenzene diradical [19], which also exhibits a large electronic delocalization.

More interesting is the observation for diradical **1** of a weak absorption at 900 nm ($\varepsilon = 2000$), which is not observed for simple polychlorotriphenylmethyl radicals nor for simple ferrocene units. Two weak bands at 325 and 440 nm dominate the spectrum of ferrocene [20]. The shorter wavelength band ($\lambda = 325$ nm) is assigned to $Fe(d\pi) \rightarrow Cp(\pi^*)$ charge transfer, $\pi \rightarrow \pi^*$ transitions, or a combination of these, whereas the longer wave-

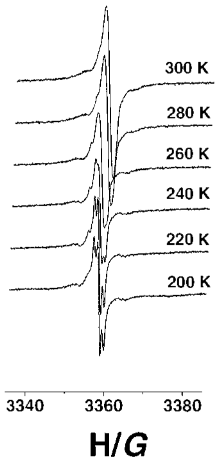


Fig. 3. Temperature-variable ESR isotropic spectra of a toluene/chloroform (1:1) solution of diradical **1**.

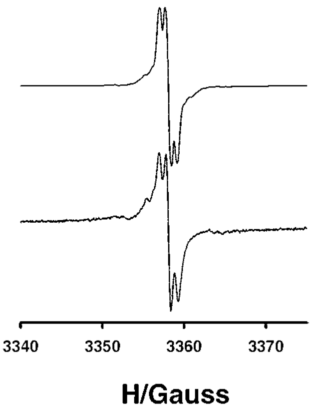


Fig. 4. Experimental (top) and simulated (bottom) isotropic solution EPR spectra of diradical **1** (right) in a toluene/chloroform (1:1) solution at 200 K.

length ($\lambda = 440$ nm) is assigned to a d-d transition within the ligand field formalism. It is true that upon substitution of one of the Cp rings of ferrocene with conjugated acceptors, one would expect changes of the visible spectra. Although the position and intensity of the ferrocene bands depends upon the nature of the chromophore acceptor group, shifts up to 520 nm and intensities of $\varepsilon = 10\,000$ have been reported. However, neither the position nor the intensity of the band appearing at 900 nm may be assigned to intrinsic ferrocene transitions. Most likely, such band may be assigned as an intervalence band transition associated with an intramolecular electron transfer from the ferrocene unit (donor) to the radical unit (acceptor). Similar intervalence band transitions have already been observed in mixed-valence complexes containing ferrocenylpyridine and rutheniumammines [21]. Moreover, the concentration-dependence of the intervalence band follows the Beer–Lambert law, confirming that the electron transfer should have an intramolecular rather than an intermolecular character.

2.4. ESR spectroscopy

X-band ESR isotropic spectra of a toluene/chloroform (1:1) solution of diradical **1** were obtained in the temperature range of 180–300 K (see Fig. 3). The poor resolution achieved at high temperatures (300–240 K) does not permit to extract any specific information about the electronic distribution of the diradical. By contrast, the resolution increases considerably at low temperatures (240–190 K) showing the lines corresponding to the coupling of the unpaired electron with the different nuclei with non-zero magnetic moments; i.e. with ^{1}H and naturally abundant ^{13}C isotope at the α and aromatic positions.

The experimental and simulated spectra of diradical **1** at 220 K are compared in Fig. 4. Computer simulation gave the isotropic g-values (g_{iso}) and the isotropic hyperfine coupling constants (a_{i}) of the unpaired electrons with the different nuclei with nonzero magnetic moments. The g_{iso} value for diradical **1** is 2.0028, which is very close to that observed for other polychlorotriphenylmethyl radicals [18]. More interesting is the comparison of the isotropic hyperfine coupling constant values with the hydrogen atoms of the ethylene moieties and some of the carbon nuclei of the triphenylmethyl unit. The values of the coupling constants of diradical **1**, $a(^1\text{H}) \approx 0.80$ G (2H), $a(^1\text{H}) \leq 0.30$ G (2H), $a(^{13}\text{C}) \approx 13.0$ G (1 C$_\alpha$) and $a(^{13}\text{C}) \approx 6.0$ G (1 C$_{\text{bridge}}$) are approximately half than those found for the related ferrocenyl monoradical **2**, $a(1^1\text{H}) \approx 1.77$ G (1H), $a(1^1\text{H}) \approx 0.57$ G (1H), $a(^{13}\text{C}) \approx 29.0$ G (1 C$_\alpha$), and $a(^{13}\text{C}) \approx 11.0$ G (1 C$_{\text{bridge}}$). It is then possible to conclude that the two electrons in diradical **1** are magnetically interacting with an exchange coupling constant, J, that fulfills the following condition $|J| \gg |a_{\text{i}}|$.

In agreement with this result, the spectrum of diradical **1** in a frozen toluene/CH$_2$Cl$_2$ (1:1) mixture shows the characteristic fine structure of a triplet species. The zero-field splitting parameters obtained by computer simulation of the spectra obtained at 160 K are $|D'| = 48$ G and $|E'| = 0$, indicating that this complex has a low (if any) anisotropy. The forbidden $\Delta m_{\text{s}} = \pm 2$ transition characteristic of triplet species, is also observed at the half-field region of the spectrum and the intensity of the corresponding signal (I_{pp}), obtained by double integration, was measured in the 4–100 K temperature region. Since the quantity $I_{\text{pp}}T$ is proportional to the population in the triplet state, the fact that $I_{\text{pp}}T$ (Fig. 5) increases with decreasing temperature indicates that the ground state of **1** is the triplet state and the singlet state should be associated with a thermally accessible excited state. A separation of $+10$ K (7 cm^{-1}) between both states was obtained from the fitting of the $I_{\text{pp}}T$ versus T plot to the Bleaney–Bowers equation [22].

2.5. Semiempirical calculations

In order to understand why the ferrocene unit acts as a ferromagnetic coupler in diradical **1**, we have performed ZINDO/1 semiempirical calculations. It should be noted that full geometry optimization with configuration interaction (CI) is an extremely time demanding process, especially when a large number of heavy atoms are involved (as is the case for diradical **1**). A reasonable alternative consisted in carrying out the geometry optimization with an UHF wave-function. The optimized structures is then used as input geometries for a single-point CI calculation, which allowed a more accurate estimation both of the electronic properties, molecular orbitals and energy minima. The optimized structure of diradical **1** obtained in such a way (Fig. 6) has an extended S-shaped profile that is very close to that of an ideal centrosymmetrical molecule with an inversion center on the metal nucleus. Such profile results in a significantly large through-space distance between the two radical centers (19 Å). The dihedral angles of the inner aromatic group of the triphenylmethyl units, with respect to their adjacent vinylene moieties, are 28.2 and 29.1°, which deviates from coplanarity. In addition, the two vinylene moieties are bent and twisted out of the plane defined by the Cp rings with small dihedral angles of 4.9 and 8.3°.

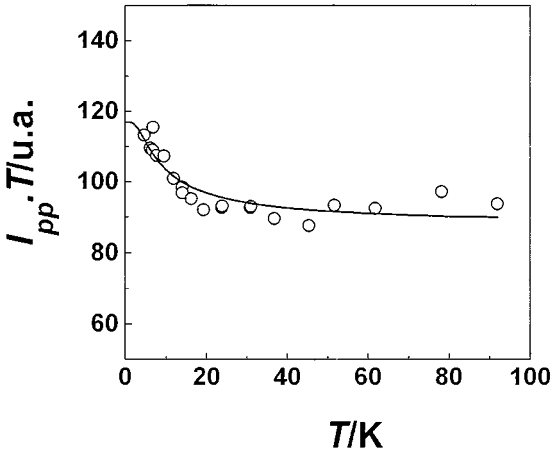


Fig. 5. Temperature dependence of the $I_{pp}{\cdot}T$ of diradical **1**. The closed circles represent the experimental data and the continuous lines the fit of experimental data to the Bleaney–Bowers equation.

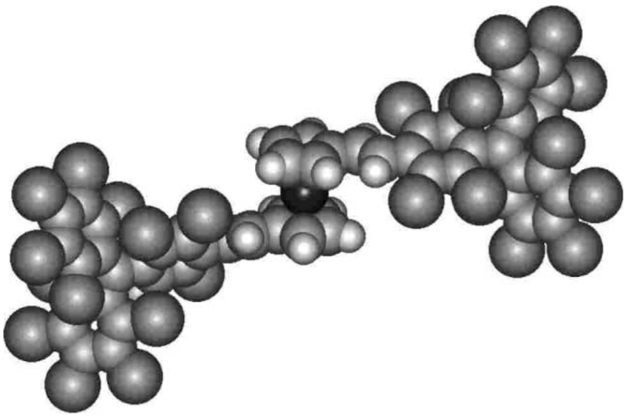


Fig. 6. ZINDO/1 semiempirical optimized structure of diradical **1**.

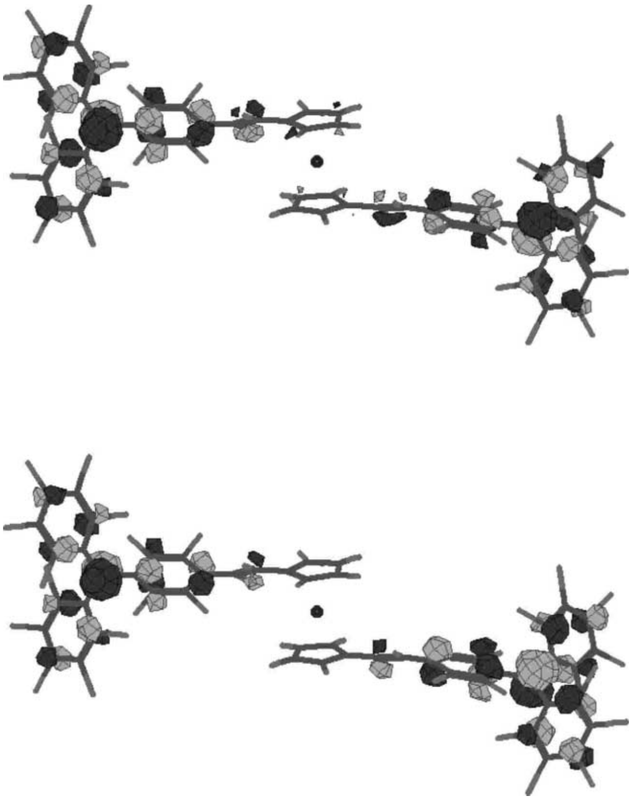


Fig. 7. Representations of the two SOMO orbitals of diradical **1** according to ZINDO/1 calculations.

The ferromagnetic coupling of the unpaired electrons of diradical **1** to give a triplet ground state can be justified in terms of elementary molecular orbital considerations. Indeed, the key to predict the spin multiplicity of an organic biradical from a molecular orbital viewpoint is to determine whether the singly occupied molecular orbitals (SOMOs) have (non-disjoint) or do not have (disjoint) coefficients on a common set of atoms, since this is a prerequisite for Coulombic repulsion between the two electrons to become operative. If the SOMOs orbitals are non-disjoint and degenerate, then the Pauli exclusion principle favors the parallel spin alignment stabilizing the high-spin state. In the case of diradical **1**, the SOMO orbitals not only are almost degenerated with an electronic energy difference less than 0.05 eV, but they are also coextensive in most part of the molecule justifying the high-spin ground state experimentally observed (Fig. 7).

3. Conclusions

Diradical **1** consisting of two polychlorinated triphenylmethyl radicals connected by a 1,1′-ferrocenylendivinylene bridge, has been synthesized and characterized. Interestingly, ESR experiments showed that the 1,1′-ferrocenylene bridge acts as a ferromagnetic coupler of two radical units connected to it. This result was justified theoretically by ZINDO/1 semiempirical calculations. The use of ferrocene as a ferromagnetic coupler can be extended to the synthesis of novel high-spin metallocene complexes bearing other open-shell organic and inorganic units providing a valuable access to this interesting class of materials.

4. Experimental

4.1. General procedures

All solvents were reagent grade from SDS and were used as received and distilled otherwise indicated. All reagents, organic and inorganic, were of high purity grade and obtained from E. Merck, Fluka Chemie and Aldrich Chemical Co. Elemental analyses were obtained in the Servei de Microanalisi del CID (CSIC), Barcelona.

EPR spectra were recorded on a Bruker ESP-300E spectrometer operating in the X-band (9.3 GHz). Signal-to-noise ratio was increased by accumulation of scans using the F/F lock accessory to guarantee a high-field reproducibility. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturation and magnetic field overmodulation were taken. To avoid dipolar broadening, the solutions were carefully degassed three times using vacuum cycles with pure argon. The g values were determined against the DPPH standard ($g = 2.0030$). Electrochemical experiments were performed with an Electromat 2000 system (ISMP Technologies), using a platinum wire as working electrode and a saturated calomel electrode (Ag/AgCl) as reference electrode. Anhydrous CH_2Cl_2 was freshly distilled over P_2O_5 under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte. UV–vis and near-IR were recorded using a Varian Cary 05E spectrophotometer. The ^{1}H-NMR spectra were recorded with Bruker FT80 spectrophotometer (^{1}H-NMR 80 MHz).

The geometry of diradical **1** was minimized using ZINDO/1 semiempirical calculations. These calculations were performed using the HyperChem 5 molecular modelling package. The initial input geometries (excluding the propeller-like arrangement of each triaryl moiety) were kept planar, i.e. the dihedral angles defined by the vinylene moieties and the phenylene rings were set to 0°. Moreover, for each diradical, two different initial input conformations differing by a 180° rotation around one of the single bonds that connects the central phenylene unit and one of the vinylene moieties, were used. It is important to notice that independently of the input model used, the minimized geometries converged in similar close-lying minima with almost identical structures.

*4.2. (E,E)-1,1′-Divinylferrocene-β,β′-ylene-bis-(4-tetradecachlorotriphenylmethane) (**4**)*

Potasium-*tert*-butoxide (46 mg, 376.4 μmol) and {4-[bis(2,3,4,5 - pentachlorophenyl)methyl] - 2,3,5,6 - tetrachlorobenzyl}(triphenyl)-phosphonium bromide monoadduct (**3**) (395 mg, 340.44 μmol) were suspended in ca. 10 ml of dry THF. The yellow ylide suspension that formed immediately was stirred for 70 min. Then the ferrocene 1,1′-biscarbaldehyde (39 mg, 160 μmol) was added and the system was stirred for a further 72 h. The reaction mixture was quenched with 5 ml of 2 N HCl and extracted with four portions of 25 ml of chloroform. The organic layer was washed with 20 ml of water, dried with $NaSO_4$ and evaporated under reduced pressure. Finally, chromatographic purification with silica and *n*-hexane/$CHCl_3$ (1:1) yield 145 mg (53.3 %) of pure **4**.

Anal. Calc. for $C_{52}H_{14}Cl_{28}Fe$·: C, 37.02; H, 0.84. Found: C, 37.06; H, 0.72%. ν_{max}(KBr)/cm^{-1}: 2925, 1634, 1533, 1369, 1338, 1299, 1241, 1138, 1045, 960, 810, 715, 685, 649, 531, 479. ^{1}H-NMR ($CDCl_3$, Me_4Si): 4.44 (s, 4H, cyclopentadienyle subst.), 4.51 (s, 4H, cyclopentadienyle subst.), 6.69 (d, 2H, $J_{trans} = 10.8$ Hz, vinyle), 6.94 (d, 2H, $J_{trans} = 10.8$ Hz, vinyle), 7.03 (s, 1H, methane).

*4.3. (E,E)-1,1′-Divinylferrocene-β,β′-ylene-bis-(4-tetradecachlorotriphenylmethyl) diradical (**1**)*

Tetrabutylammonium hydroxide (40% in water, 1.5 M, 131 μl, 197 μmol) was added to a solution of **4** (133 mg, 78.8 μmol) in 15 ml of THF. The solution, which immediately turned purple was stirred at room temperature (r.t.) for 4 h. Subsequent oxidation of the resulting dianion with *p*-chloranil (53.6 mg, 220 μmol) was performed and the resulting solution was left at r.t. for 35 min. Finally the solvent was eliminated under reduced pressure and the product was purified by column chromatography using hexane in silicagel tetrachlorocarbon (1:1) to yield 60 mg (45.2%) of pure **1**.

Anal. Calc. for $C_{52}H_{12}Cl_{28}Fe{\cdot}2C_6H_6$: C, 41.80; H, 1.40. Found: C, 42.20; H, 1.65%. ν_{max}(KBr)/cm^{-1}: 2923, 2853, 1716, 1623, 1507, 1645, 1337, 1319, 1261, 1156, 1119, 1046, 959, 945, 869, 817, 735, 712, 699, 652, 561, 530, 475, 417.

Acknowledgements

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