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Synthesis and Characterization of a Nanoscopic Molecular-Scale Wire Bearing Terminal Redox-Active Polychlorotriphenylmethyl Radicals

Olaf Elsner, Daniel Ruiz-Molina, José Vidal-Gancedo, Concepció Rovira,* and Jaume Veciana*

Institut de Ciencia de Materials de Barcelona (CSIC),
Campus Universitari de Bellaterra, 08193-Cerdanyola, Spain

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ABSTRACT

The synthesis and characterization of a new nanoscopic diradical species with a long radical-to-radical distance of 3.2 nm, are reported. Intramolecular electron-transfer phenomena in the radical anion derived from the partial reduction of such diradical are studied by optical and ESR spectroscopies. These experiments showed a very small or negligible electronic coupling between the two terminal redox sites due to strong localization effects associated to the excellent electron acceptor ability of polychlorotriphenylmethyl radicals.

The possibility of integrating molecular-scale wires in conventional circuits may drive an impressive advance of microelectronics and computation. As pointed out by Tour et al.,[1] the interest in and technical advantages of such integrated molecular-scale devices are notable because of their reduced sizes and faster intramolecular electron transfer (IET) rates, when compared to conventional microchip components.[2] Recently, different groups have demonstrated the existence of direct electronic conduction through single molecules,[3] which leads us to expect practical applications for this type of molecular systems in the future. However, if a truly molecular computational device is to be achieved, new systematic studies of simple models that allow us to obtain the limits and rules for the prediction and control of the electron propagation in molecular wires[4] are highly necessary.

Mixed-valence compounds are excellent candidates for such studies because IET phenomena can be easily characterized by the effective electronic coupling between the electrophores located at the terminal sites of the compound. This electronic coupling is measured by the V_{ab} parameter, which has the dimension of energy (in cm^{-1}). This parameter can be experimentally determined from the position, intensity, and width of the intervalence transition band of the electronic absorption of the compound, which generally occurs in the visible or near-infrared region.[5] Most of the mixed valence complexes that have been shown to exhibit intervalence transition bands are homo and heteronuclear metallic complexes,[6] in which the two metal atoms with different oxidation states are connected through an organic bridging ligand. In contrast, purely organic mixed-valence compounds have so far received only limited attention, probably due to their high instability, even though their significant interest because of the high flexibility and tunability of organic synthesis.[7]

Polychlorotriphenylmethyl radicals show an astonishing thermal and chemical stability, due to the presence of bulky chlorine atoms at the *ortho* and *para* positions of the triphenylmethyl radicals.[8] Moreover, such radicals are electroactive species giving rise, either chemically or electrochemically, to the corresponding anions and cations that are also quite stable species.[9] As a consequence, it seemed interesting to obtain and study symmetrical molecules consisting of two of these electrophoric radicals linked with different types of bridges. These diradicals could be converted by a partial reduction to the corresponding radical-anions, and the resulting mixed-valence species therefore may display interesting long-range electron-transfer phenomena. In our group, we have already shown the convenience of using mixed-valence systems derived from polychlorinated triarylmethyl polyradicals to obtain pure organic compounds exhibiting long-range IET phenomena.[10] Here, we report the new diradical species **1** consisting of two polychlorinated triphenylmethyl units connected by a 1,4-bis(1-ethynylphenyl) benzene bridge, with a significantly large through-space radical-to-radical distance of 3.2 nm. This spacer not only

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* To whom correspondence should be addressed. E-mail: vecianaj@icmab.es

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ensures a high degree of rigidity but it has already been shown to have a suitable electronic structure to promote strong electronic coupling between chain ends separated by a large distance.[11]

The synthetic route for preparing diradical **1** is based on two main steps. The first step is the synthesis of the bis(triphenylmethane) **6** by a bisWittig reaction, whereas the second step is the generation of the corresponding dicarbanion by an acid−base reaction followed by the subsequent oxidation of such dicarbanion to the corresponding diradical (see Scheme 1). Initially, compound **4** was obtained by a palladium catalyzed coupling of *p*-diethynylbenzene and two equivalents of 4-bromobenzaldehyde. Once compound **4** was synthesized, it was coupled with two equivalents of the phosphonium bromide derivative **5**[10a] by a Wittig reaction to give the corresponding bis(triphenylmethane) **6**, the precursor of diradical **1**. Finally, the synthesis of diradical **1** was undertaken by treatment of the corresponding precursor with an excess of $n\mathrm{Bu_4N^+OH^-}$ and subsequent oxidation of the resulting dicarbanion with *p*-chloranil.[12] This diradical is completely stable in air both in the solid state and in dilute solutions. Despite the recurrent use of different crystallization techniques, obtaining crystals suitable to determine the X-ray structure of **1** remained elusive.

Scheme 1

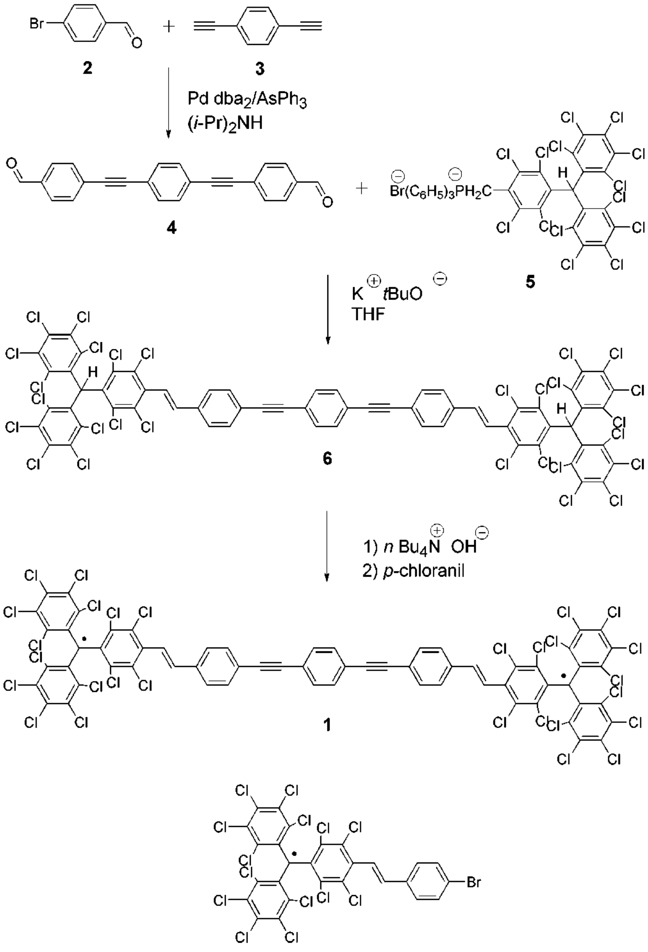

Figure 1. AM1 semiempirical optimized structure of diradical **1**.

To analyze the structural conformation of diradical **1**, semiempirical AM1 calculations were carried out. The resulting minimized geometry is shown in Figure 1. The AM1 optimized structure of diradical **1** has an extended profile that results in a significantly large through-space distance between the two electron active sites of 3.2 nm and a molecular end-to-end distance of 4.1 nm. As far as intramolecular electron-transfer phenomena are concerned, the main distance to be considered is the through-bond distance between the two electron active sites, that is, the sum of bond lengths corresponding to the conjugated pathway. Such distance, measured from the two radical alpha carbon atoms is 40.5 Å. Although the central aromatic rings are slightly twisted, the three aryl rings do not differ considerably from coplanarity. This is a feature previously observed[13] in the crystalline structure of the molecule (*p*,*p*)-$\mathrm{HSC_6H_4C{\equiv}CC_6H_4{\equiv}CC_6H_5}$, which would facilitate the electron transmission through the π−delocalizing conjugated bridge connecting the two radical units.[14]

Electrochemical studies in $\mathrm{CH_2Cl_2}$, with $n\mathrm{Bu_4NPF_6}$ (0.1 M) as a supporting electrolyte (vs SCE) and using a Pt wire as a working electrode, were done at room temperature. The cyclic voltammogram (CV) of diradical **1** shows only one reversible reduction process at a constant potential of approximately −0.13 V (vs SCE), despite the presence of two electronically active triphenylmethyl units. The two standard redox potentials expected for this diradical, due to the conjugation of the bridge, must be very close and as a consequence, a single two-electron wave, with minor differences in shape with respect to a true bielectronic process, is observed.

X-band ESR spectra were obtained at different temperatures (from 180 to 293 K) in $\mathrm{CH_2Cl_2}$/toluene. The spectrum at room temperature shows three overlapped lines corresponding to the coupling of the unpaired electrons with two equivalent ^{1}H nuclei (one hydrogen atom of each ethylene unit of the molecule), along with other satellite lines due to the coupling with the different nuclei with nonzero magnetic moments, that is, the naturally abundant ^{13}C nuclei. Computer simulation gave the isotropic *g*-value (g_{iso}) and hyperfine coupling constants (a_i). The experimental and simulated ESR spectra of diradical **1** are compared in Figure 2 (left). The g_{iso} value is 2.0028, and the values of the coupling constants are $a(^1\mathrm{H}) \approx 0.88$ G (2H), $a(^{13}\mathrm{C}_\alpha) \approx 13.0$ G, $a(^{13}\mathrm{C}_{\mathrm{bridge}}) \approx 6.3$ G, and $a(^{13}\mathrm{C}_{\mathrm{ortho}}) \approx 5.1$ G. At this point, it is important to emphasize that the resulting coupling constants are approximately half the value of those found for related polychlorotriphenylmethyl monoradical species.[7−8] For instance, the ESR spectrum of radical **7** at 300 K displays two main symmetrical lines,[9] which are originated by the hyperfine coup-

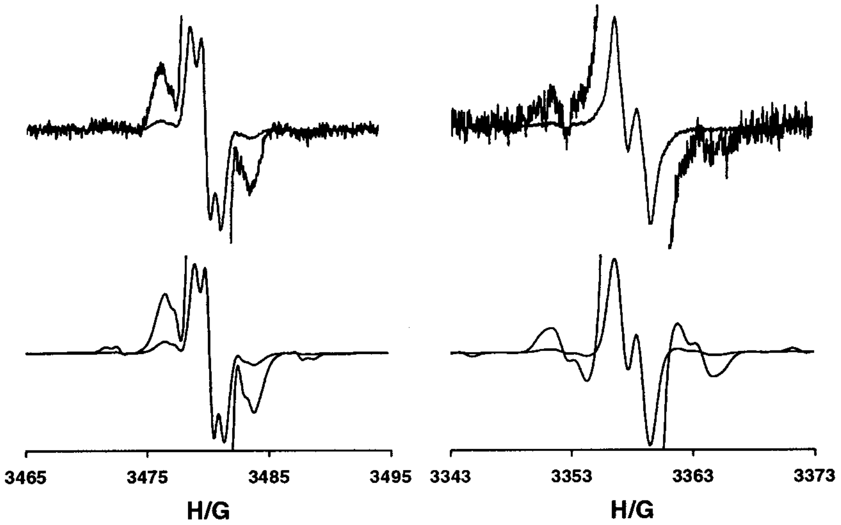

Figure 2. Experimental (top) and simulated (bottom) isotropic solution EPR spectra of diradical **1** (left) and radical anion $\mathbf{1}^{-\bullet}$ (right).

ling of the unpaired electron with one hydrogen atom of the ethylene moiety with a coupling constant value of $a(^{1}\text{H}) \approx 1.80$ G (1H). This spectrum also shows satellite lines with $a(^{13}\text{C}_{\alpha}) \approx 29.5$ G, $a(^{13}\text{C}_{\text{bridge}}) \approx 13.0$ G, and $a(^{13}\text{C}_{\text{ortho}}) \approx 10.7$ G. 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, $J \gg a_i$. The spectrum of diradical **1** in a glassy frozen toluene/CH_2Cl_2 (1:1) mixture did not show either the fine structure or the forbidden $\Delta m_s = \pm 2$ transition characteristic of a triplet species. On the contrary, a single broad line, which can be simulated with the zero-field splitting parameters $|D'| < 3$ G and $|E'| \approx 0$ G, was obtained. The lack of a fine structure and the $\Delta m_s = \pm 2$ transitions for this species is in accordance with the rapid fall down of the $|D'|$ value with the effective distance of the two unpaired electrons.[15]

The magnetic susceptibility of a solid sample of radical **1** was measured in the temperature range of 2 to 200 K. At 200 K, the χT vs T plot is characterized by a χT value of 0.78 emu.K.mol^{-1}, which is very close to the spin-only value expected for two radicals exhibiting a very weak exchange interaction. This value is maintained approximately constant down to 20 K, whereupon it decreases. Because the quantity χT is proportional to the population in the triplet state, the fact that χT decreases with decreasing temperature indicates that the ground state of **1** is the singlet state, and the triplet state should be regarded as a thermally accessible excited state. A separation of 1.5 K between both states was obtained from the fitting of the experimental data to the Bleaney—Bowers equation.[16] The weak antiferromagnetic interaction between the two spins of this compound is in agreement with the topology—p,p' connectivity—of this nondisjoint Kekulenic hydrocarbon and with the long effective distance of the two radical sites.

The generation and study of the mixed-valence species $\mathbf{1}^{-\bullet}$ was done using a spectroelectrochemical methodology previously described.[17] Such methodology is based on the coulombimetric reduction of diradical **1** and the simultaneous observation of the corresponding electronic absorption spectra, regularly recorded during the reduction process for different values of the average number (n) of electrons added, where $0 \leq n \leq 2$. These studies evidenced the lack of any intervalence band transition originated by the presence of an IET phenomenon. One possible reason is that the intervalence transition appears as a very broad tail on the edge of a nearby electronic transition or even completely masked. For this reason, variable-temperature ESR spectra of a solution of $\mathbf{1}^{-\bullet}$ were also recorded. The spectrum at low temperature (200 K) displays two main lines corresponding to the coupling of the unpaired electron with only one ^{1}H along with another satellite lines due to the coupling with the naturally abundant ^{13}C nuclei (Figure 2, right). Computer simulation gave a g_{iso} value of 2.0025, which is very close to that observed for diradical **1**. More interesting is the comparison of the isotropic hyperfine coupling constant values of $\mathbf{1}^{-\bullet}$, $a(^{1}\text{H}) \approx 1.6$ G (1H), $a(^{13}\text{C}_{\alpha}) \approx 29.3$ G, $a(^{13}\text{C}_{\text{bridge}}) \approx 12.3$ G, and $a(^{13}\text{C}_{\text{ortho}}) \approx 10.2$ G, which are approximately double the value of those found for diradical **1**. This result demonstrates that at low temperatures, the unpaired electron of $\mathbf{1}^{-\bullet}$ is localized, on the ESR time scale, only on one-half of the molecule, that is, on one stilbene-like moiety. An increase of the temperature may lead to the presence of a thermally activated electron-transfer phenomenon. If this is the case, the ESR spectra of $\mathbf{1}^{-\bullet}$ will reflect the coupling of the unpaired electron with the two ^{1}H nuclei of the two stilbene-like moieties and consequently, an ESR spectrum similar to that observed for diradical **1** should appear. However, when the temperature of a solution of $\mathbf{1}^{-\bullet}$ is increased up to 400 K, no evolution of its corresponding ESR spectra is observed confirming that, at least in the temperature range studied, the IET does not take place. This result, together with the lack of an intervalence band transition in the absorption spectra, suggests that there is a localization effect of the extra electron in the radical-anion species $\mathbf{1}^{-\bullet}$.

Why do we have a localized electronic structure for $\mathbf{1}^{-\bullet}$ when poly(phenylethynyl) bridges have been shown to be good electronic conductors at the molecular level and the topology of the two redox units is the correct one for enhancing the electronic interaction? Certainly, the use of a long bridge (3.2 nm) is expected to attenuate the electronic conductivity through the π-orbitals involved in the electron-transfer process. However, electron-transfer phenomena are still effective in systems consisting of ferrocene groups attached to gold electrodes via oligo(phenylethynyl) bridges ranging from a few Angstroms to 43 Å.[11b] Then, the excellent electron acceptor ability of polychlorotriphenylmethyl radicals is proposed as the main explanation of the substantial localization of the extra electron on one of the radical units of $\mathbf{1}^{-\bullet}$.[18] Indeed, the extra electron of the mixed-valence species $\mathbf{1}^{-\bullet}$ will tend to spend less time on the poly(phenylethylene) bridge when it is flanked by such excellent electron acceptor electrophores, increasing the energy barrier associated with the electron-transfer process. Therefore, in nanoscopic molecular-scale systems with terminal redox-active centers, there seems to be a subtle interplay between the acceptor ability of the electrophore unit and the size and nature of the bridge that makes feasible or not the long-range electron-transfer phenomena. One of the possible approaches that one might follow to improve the electronic coupling in this type of systems is the intercalation of an electronic relay.[19] Such a unit, which should have a strong acceptor ability as well, is expected to activate the electron transfer by modulation of the energy of the π-conjugated pathway. Future work to synthesize new nanoscopic molecules bearing terminal redox-active polychlorotriphenylmethyl radicals connected through a long rigid π-conjugated bridge with an electronically active relay unit are currently underway.

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