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Synthesis, electrochemical behavior and magnetic properties of polyradicals of the TTM series

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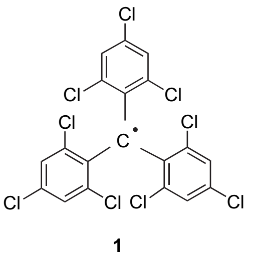
Abstract—Condensation reactions between (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical and a new hexafunctionalized radical of the TTM series, tris(3,5-dichloroformil-2,4,6-trichlorophenyl)methyl radical or its corresponding diamagnetic precursor **6** yield macromolecular heptaradical **3** and hexaradical **4**, respectively, with high magnetic purity. Both solid polyradicals show stability in nitrogen at temperatures up to 300 °C and in solution their electronic absorptivities do not decrease appreciably for weeks. EPR studies of both polyradicals in solution suggest that unpaired electrons are exchange coupled, and at low temperatures they show weak dipolar spin–spin couplings. Their electrochemical behavior was analyzed by cyclic voltammetry and differential pulse voltammetry. Heptaradical **3** is reduced in seven-electron two-stage processes, and oxidized in seven-electron one-stage process.

1. Introduction

Nowadays many efforts are focused in the field of organic magnetic molecules as materials with attractive potential applications in different areas such as magnetic imaging and magneto-optics.[1] One of the advantages of the use of organic molecules instead of inorganic based materials lies in the possibility of chemical modification onto the molecule affecting their electronic properties and allowing the modulation of the dipolar interactions between the different magnetic centers. An important requirement to design and prepare high-spin organic molecules is a strong π-conjugated coupling between unpaired electrons. One rational approach for it consists in dividing the high-spin molecule into two components: the spin-containing (SC) fragment, which provides the unpaired electron and the ferromagnetic coupling (FC) for connecting the different radical centers ferromagnetically.[2] Many of the SC fragments are based on triarylmethyl radicals, which have been the object of increasing interest in the last years and many high-spin species based on them as building blocks have been reported.[3,4] On the other hand, the amide bond –N–CO– as a FC unit has shown to be an exchange coupler between spin centers due to the double bond character of the N–C bond allowing the extension of π-conjugation between spin-bearing moieties.[5] The stability is another essential requirement to consider in magnetic organic molecules. Radicals of the TTM [tris(2,4,6-trichlorophenyl)methyl (**1**)] series are very stable carbon-centered radicals whose persistence is conferred by the presence of six aromatic chlorines surrounding the trivalent carbon atom.[4] These organic radicals are completely unassociated as crystalline solids with no appreciable decomposition both in solid and in solution. Consequence of this stability is the feasibility to incorporate the amide function by condensation of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**2**), a functional radical of the TTM series, with different acid chlorides without impairment of the radical character of the molecule.[4b]



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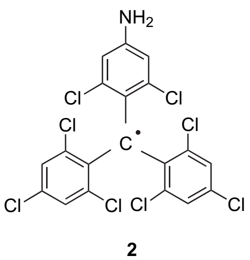

2

This article describes the synthesis and magnetic properties of two macromolecular-branched polyradicals **3** and **4** with amide functions as linker for connecting several triphenylmethyl radicals of the TTM series. These polyradical species are composed of a central triphenylmethyl radical or its diamagnetic precursor as the core of the dendrimer and three

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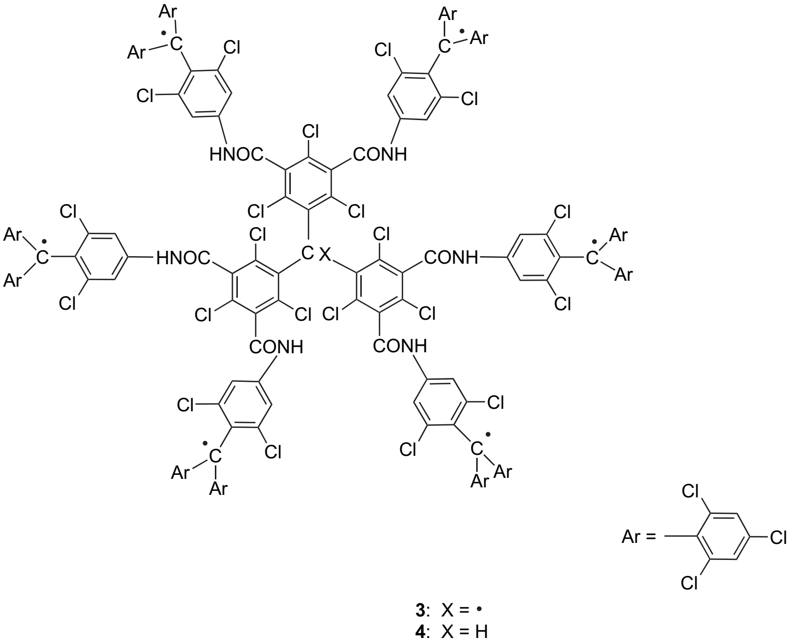
pairs of peripheral triphenylmethyl radicals, each pair connected to one of the phenyl groups of the core through amide functions as linkers employing a *meta*-topology. This arrangement of the radical centers in the macromolecule, characterized by larger dimensions than that of linear systems, guarantees the in-phase periodicity of the spin polarization in the π-orbitals as a consequence of each radical center in the macromolecule to make feasible the generation of high-spin systems. Besides the magnetic properties of these organic molecules, radicals of the TTM series are redox units and they are electrochemically reduced and oxidized in reversible processes. Chemically they behave as oxidants in the presence of electron-rich species to give stable negatively charged species, by electron transfer processes, which yield the corresponding diamagnetic triphenylmethanes in the presence of proton-donors. In addition, they participate as electron-donors in front of oxidants to yield the stable carbocations.[4d] Therefore, radicals of the TTM series are species of fundamental importance in the study of single-electron transfer reactions, as well as in the investigation of reaction mechanisms. Consequently, the new polyradicals described in this article will be the electroactive materials with several redox units that can accept or transfer multiple number of electrons under specific applied potentials. Therefore, we also report the redox properties of these polyradicals.



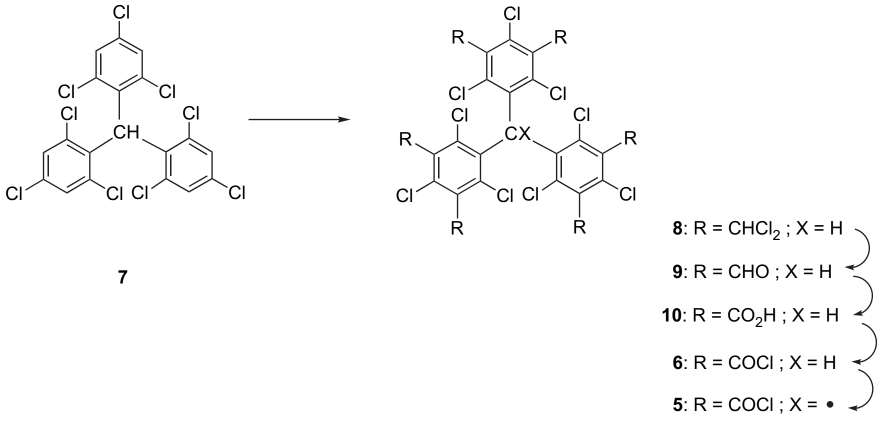
3: X = •
4: X = H

2. Results and discussion

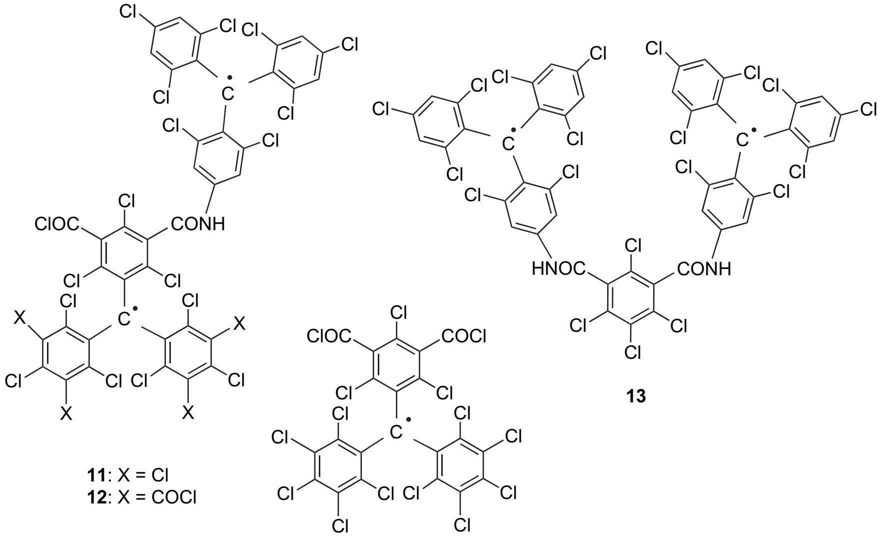
2.1. Synthesis and stability

Heptaradical **3** and hexaradical **4** have been prepared by multiple condensations of amino radical **2** with the hexavalent tris(3,5-dichloroformil-2,4,6-trichlorophenyl)methyl radical (**5**) and its diamagnetic parent hydrocarbon **6**, respectively, without impairment of the radical character of all trivalent carbon atoms. Radical **5** was generated by well-known and simple synthetic route following the sequence outlined in Scheme 1.

Dichloromethyl groups in tris($\alpha,\alpha,\alpha',\alpha'$,2,4,6-heptachloroxylyl)methane (**8**) were introduced by alkylation of tris(2,4,6-trichlorophenyl)methane (**7**) with chloroform in the presence of $AlCl_3$ by means of Friedel–Crafts reaction as reported.[6] An acid hydrolysis of hydrocarbon **8** with sulfuric acid gives **9** with six carboxyaldehydes in all *meta* aromatic positions. Oxidation of aldehydes to carboxylic acids with CrO_3 yields triphenylmethane **10**, which affords **6** by treating with thionyl chloride. Finally, radical **5** was generated by treating **6** with tetrabutylammonium hydroxide to give the anion followed by oxidation with chromium(VI) oxide. Condensation of an excess over 6:1 of radical **2** with **5** or **6** in boiling benzene and in the presence of cesium carbonate takes place without impairment of the radical character of the magnetic species, as observed in the benzoylation of radical **2** with benzoyl chloride.[4b] Thus, the multiple magnetic character of **4** with six trivalent carbon atoms and of **3** with seven trivalent carbon atoms is retained. To know more thoroughly the dipolar interactions among electronic spins in simpler model systems with only two unpaired electrons, the synthesis of the three new biradical species, **11**, **12** and **13**, was performed. Biradicals **11** and **12** result from the monocondensation reaction between amino radical **2** and bis(pentachlorophenyl)[2,4,6-trichloro-3,5-bis(chlorocarbonyl)phenyl]methyl radical (**14**) and radical **5**, respectively. The electronic exchange and dipolar interactions in both biradicals **11** and **12** will confirm the amide function as a good linker of two SC fragments. In the same way, biradical **13**, product of condensation between 2,4,5,6-tetrachloroisophthaloyl dichloride and amino radical **2** in a 1:2 molar proportion, will give information of electronic spins between the two peripheral triphenylmethyl moieties in hexaradical **4** and heptaradical **3** linked through two amide functions.



Scheme 1.



11: X = Cl
12: X = COCl

13

14

Polyradicals **3** and **4** are stable in air, either in solution or in solid form. Their stability is mainly due to steric shielding of the six *ortho* chlorine atoms around each radical center, which forces torsional displacements from planarity of the aromatic planes around the sp^2 carbon atom. This effect justifies the poor delocalization of the single electron into the aromatic substituents, similar to all free radicals of the TTM series.[4a,b] The electronic absorption spectra of **3** and **4** in CH_2Cl_2 solution display the characteristic bands of the radical character of the molecules, with absorptivities approximately seven and six times for **3** and **4**, respectively, as high as those of monoradical species of the same TTM series [λ (ε, $dm^3\ mol^{-1}\ cm^{-1}$), **3**: 376 (191,500), 514 (8330), 557 (8230) nm; **4**: 376 (168,500), 512 (5800), 553 (5880) nm] and their absorptivities do not decrease appreciably for weeks. In situ oxidation with an excess of $SbCl_5$ resulted in the generation of the stable and highly blue solutions of the multiple charged cations $\mathbf{3}^{7+}$ [λ (ε) 568 (sh) (160,140), 670 (331,940) nm] and $\mathbf{4}^{6+}$ [λ (ε) 564 (sh) (136,800), 668 (264,270) nm].

2.2. Electron paramagnetic resonance

X-band EPR spectrum of the hexafunctional radical **5** was recorded in deoxygenated CH_2Cl_2 solution (~10^{-3} M) at 193 and 298 K. The spectrum at 193 K showed a single line centered at g=2.0033 with a peak-to-peak line width ΔH_{pp}=1.0 G. At high gain values the isotropic coupling with the ^{13}C (natural abundance, 1.07 %) nuclear spins of the three bridgehead carbons and the six *ortho*-carbons appeared on both sides of the central line at 9.75 and 13.0 G, respectively. At 298 K, the pair of bands equidistant of the central line and associated with the ^{13}C nuclear spins of α-carbon atom was well observed in the spectrum with a coupling value of 29.4 G.

The spectrum of biradical **11** in deoxygenated CH_2Cl_2 solution (~10^{-3} M) and recorded at room temperature gave a single and broad line (g=2.0035, ΔH_{pp}=2.0 G). Isotropic coupling with the naturally abundant ^{13}C nuclei is only appreciable at high gains with the α-carbon atom and its value, $a(\alpha^{13}C)$~13 G, is approximately half the value found in monoradical species of the TTM series, suggesting that the electron-exchange interaction is larger than the hyperfine interaction, ($|J|>|a_i|$). Figure 1 shows the evolution of the spectra of biradical **11** in 2-methyltetrahydrofuran (MTHF) at temperatures from 270 K down to 120 K. This effect is due to the anisotropic dipolar electron–electron interaction and at intermediate temperatures when the solution is not

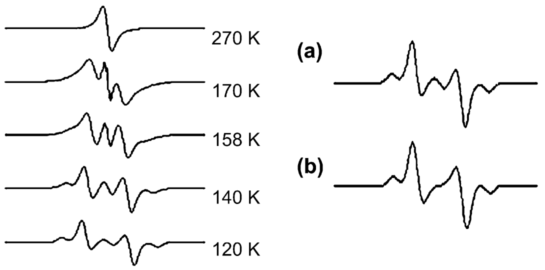


Figure 1. Left: a series of EPR spectra of a solution of biradical **11** in MTHF from 270 K down to 120 K, showing the intensity dependence of the dipolar electron–electron interaction. Right: (a) experimental spectrum of biradical **11** in MTHF at 120 K. (b) Simulated spectrum using the values of the zero-field parameters *D* and *E* given in the text.

glassy yet, the central line showed hyperfine structure due to the unresolved coupling of the six aromatic protons with a value $a(6H)=1.25$ G, very close to the coupling value in most radicals of the TTM series. Most probably, this line corresponds to some small impurities of monoradical. The fine structure showed in the spectrum at 120 K (solid matrix) provides an estimation of the zero-field parameters *D* and *E* by spectral simulation (Fig. 1, right). This spectrum is consistent with $|D/hc|=22.5\times10^{-4}\ \text{cm}^{-1}$ and $|E/hc|=0.6\times10^{-4}\ \text{cm}^{-1}$ being $g_x=g_y=2.0033$ and $g_z=2.0027$, and using a line width $\Delta H_{pp}=4.6$ G. Confirmation of the triplet state was provided by the presence of a doublet in the $\Delta m_s=\pm2$ region of the spectrum, which obeyed the Curie's law ($I\sim1/T$) between 4 and 23 K (Fig. 2), consistent with a triplet ground state or a degeneracy of singlet and triplet states. Within the magnetic dipole–dipole approximation, the experimental value *D* can provide information about the mean distance between unpaired electrons via the equation $R=(0.65g^2/D)^{1/3}$. In our case, the calculated distance is $R=10.5$ Å, which is close to 9.3 Å, a value between the centers of the two triphenylmethyl moieties estimated from molecular modeling. This similarity between both values suggests that spin densities are mainly confined in the central carbon atoms of both moieties.

The spectrum of biradical **12** in MTHF recorded at 4 K showed a multiplet very similar to that observed for biradical **11**, as expected for very close molecular structures, with the difference that the central signal is more intense. A direct comparison of the $\Delta m_s=\pm1$ for both spectra at 4 K is shown in Figure 3. The two pairs of broad lines due to the anisotropy of immobilized triplet species are practically at the same positions, and the more intense central signal in **12** may be attributed to some small monoradical impurities or to other frozen conformations with weaker electron dipolar interactions.

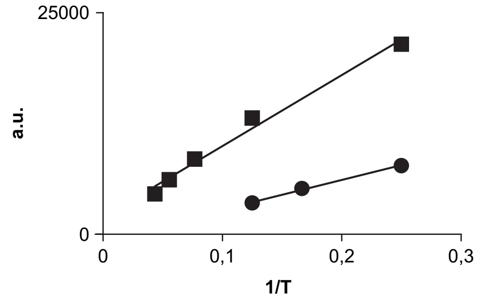


Figure 2. Temperature dependence of the $\Delta m_s=\pm2$ EPR signal intensity of the biradicals: **11** (■) and **13** (●). Solid lines are least-square fits to Curie's law.

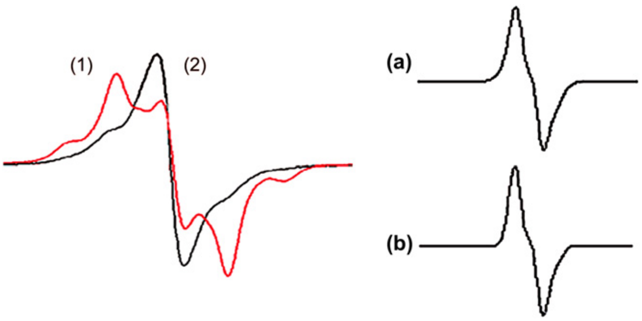


Figure 3. Left: EPR spectrum of (1) biradical **11** and (2) biradical **12** in MTHF at 4 K. Right: (a) experimental and (b) simulated spectrum of biradical **13** in MTHF at 120 K, using the zero-field parameters given in the text.

The spectrum of biradical **13** in MTHF at 120 K showed a broad signal with small inflection, which suggests a much poorer dipolar interaction between the electronic spins. Despite the lack of fine structure, we have been able to estimate the zero-field parameters by spectral simulation. Figure 3 shows the experimental and the simulated spectra using the values $|D/hc|=5.70\times10^{-4}\ \text{cm}^{-1}$ and $|E/hc|\sim0.0\ \text{cm}^{-1}$ being $g_x=g_y=2.0031$ and $g_z=2.0020$, and using a line width $\Delta H_{pp}=4.0$ G. Confirmation of the triplet state was provided by the presence of a doublet in the $\Delta m_s=\pm2$ region of the spectrum, which obeyed the Curie's law ($I\sim1/T$) between 4 and 8 K (Fig. 2), consistent with a triplet ground state or a degeneracy of singlet and triplet states. The mean distance between unpaired electrons via the equation $R=(0.65g^2/D)^{1/3}$ is $R\sim16.6$ Å and the distance estimated from molecular modeling is 13.6 Å.

The EPR spectra of MTHF solutions ($\sim10^{-4}$ M) of heptaradical **3** and hexaradical **4** at 295 K showed broad ($\Delta H_{pp}\sim4$ G) and single lines with $g=2.0030\pm5$. At high gain, these broad lines probably hamper the observation of satellite lines corresponding to the small couplings with ^{13}C nuclear spins of

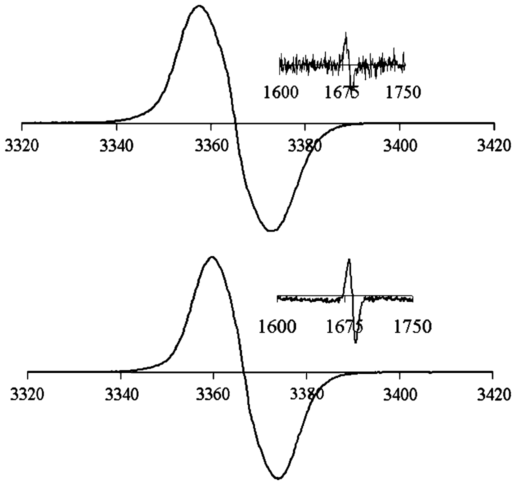


Figure 4. Up: EPR spectrum of heptaradical **3** in MTHF at 4 K; inset represents the $\Delta m_s=\pm2$ line. Down: EPR spectrum of hexaradical **4** in MTHF at 4 K; inset represents the $\Delta m_s=\pm2$ line.

the α-carbon atoms in **3** and **4**. Anyway these couplings are much lower than those of the corresponding monoradicals of the TTM series, strongly suggesting that the unpaired electrons are exchange coupled. The EPR spectra of **3** and **4** (Fig. 4) recorded at 4 K showed in the $\Delta m_s = \pm 1$ region a broad signal, $\Delta H_{pp} = 19.0$ and 18.0 G, respectively, without fine structure, and in the $\Delta m_s = \pm 2$ region a small transition characteristic of a triplet state. In both cases, it is difficult to estimate the zero-field parameters, but they should be very small suggesting low dipolar spin–spin couplings between unpaired electrons.

2.3. Magnetic measurements

Magnetization was measured in static magnetic fields 0–5 T using a SQUID magnetometer (Quantum Design model MPMS-XL). The same device was employed in the measurements of ac susceptibility in the temperature range 1.8–300 K. The ac drive amplitude and frequency were 4.5 Oe and 10 Hz, respectively. The low-temperature magnetization curves were fitted to the following parametric expressions obtained within the mean-field approximation for *n* spins with $s=1/2$ and $g=2$:

$$M = nN_A\mu_B \tanh x, \quad B = \mu_B^{-1}(kTx - k\theta \tanh x) \qquad (1)$$

M is the magnetization and *B* is the applied magnetic field induction in tesla. Here $n=6$ and 7 for **4** and **3**, respectively, *x* is a parameter running from zero to infinity. The curves calculated using Eq. 1 at $T=1.8$ (continuous line) and 5 K (dotted line) are presented in Figure 5a along with the corresponding data points. The best-fit values of θ, the only adjustable parameter in Eq. 1, are −1.2 K for the heptaradical **3** and −0.7 K for the hexaradical **4**. The small negative values of θ manifest the presence of a weak antiferromagnetic interaction.

The initial susceptibility of the two samples was fitted to the following formula:

$$\chi = nN_A\mu_B^2/k(T-\theta) + \chi_0 \qquad (2)$$

The curves calculated using Eq. 2 as well as the experimental points are shown in Figure 5b. Apart from the Curie–Weiss term, which follows naturally from Eq. 1, Eq. 2 contains a temperature-independent term χ_0. The values used in the fit were $\chi_0=0.064$ (**4**) and 0.11 emu/mol (**3**). Those rather large values account for the addition of all possible temperature-independent contributions, i.e., the sample holder capsule and cotton, typically >0 and the negative diamagnetic sample contribution, but do not affect the low temperature ($T<100$ K) analysis. In fact, as stated in what follows, the initial susceptibility data analysis also agrees very well with the expected behavior for **6** and **7** spin radicals with $s=1/2$.

The thermal variation of the effective magnetic moments per radical in **3** and **4** is given by $\mu_{\text{eff}}=\mu_B[3kT(\chi-\chi_0)/nN_A]^{1/2}$ and is shown in the insets of Figure 5b. In the range 40 K<T<100 K, μ_{eff} is slightly temperature dependent with mean values 1.70±0.03 and 1.76±0.02, for compounds **3** and **4**, respectively. These quantities are quite close to the

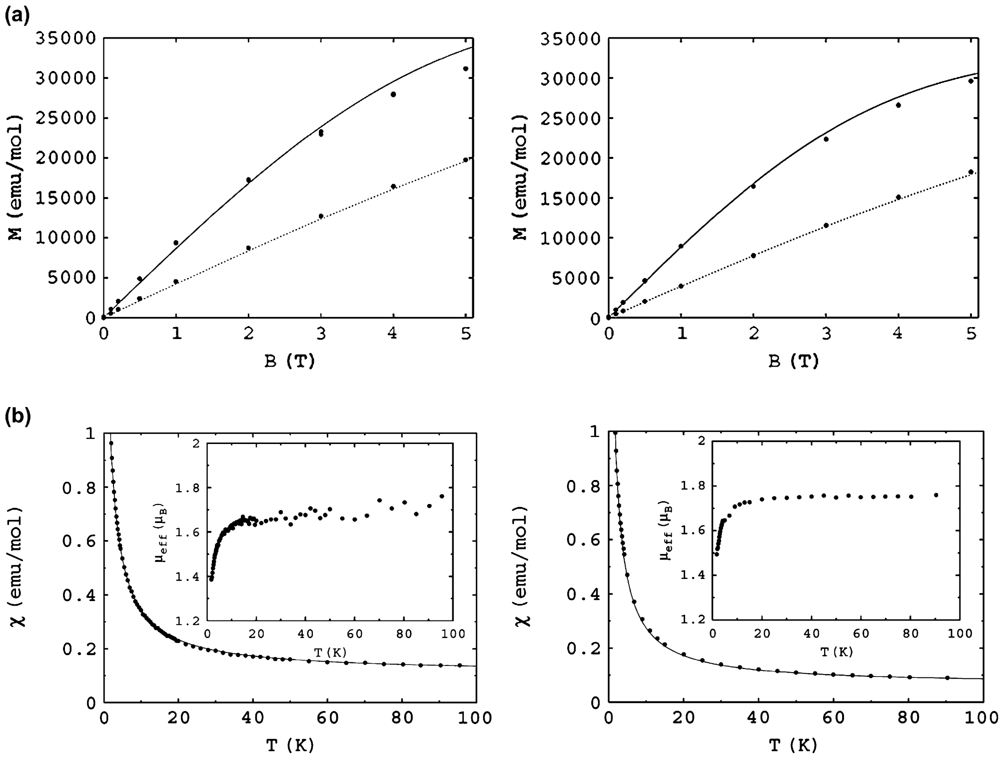


Figure 5. (a) Data points corresponding to the magnetization of polyradicals, left: heptaradical **3** and right: hexaradical **4** in solid as a function of field strength at 1.8 (upper function) and 5 K (lower function). Continuous lines calculated as indicated in the text. (b) Data points corresponding to the susceptibility of polyradicals, left: heptaradical **3** and right: hexaradical **4** as a function of temperature. Continuous lines calculated as indicated in the text. Insets show effective magnetic moments as a function of the temperature.

theoretical value of 1.73μ_B for independent radical centers and only decrease at very low temperatures. Such a behavior is characteristic of weakly intermolecular antiferromagnetic interaction.

2.4. Cyclic voltammetry

Cyclic voltammograms for the reduction of a 10^{-3} M radical **5** solution in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate on Pt showed a quasi-reversible one-electron redox pair corresponding to the process $\mathbf{5}+e^- \rightleftharpoons \mathbf{5}^-$, with a standard potential $E°$=0.16 V vs SCE (difference between the anodic and cathodic peak potentials, $E_p^a - E_p^c$=0.15 V at v=100 mV s^{-1}). The strong electron-acceptor properties of **5** denoted by the positive value of its redox potential is ascribed to the presence of six electron withdrawing substituents in aromatic *meta* positions. That is feasible because its oxidant power is much higher than that of TTM radical ($E°$=−0.66 V versus SCE)[7], but still lower than that of the tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl radical ($E°$=0.58 V versus SCE),[7] the most oxidant radical species in the TTM series so far. Figure 6a shows the cyclic voltammograms for the reduction of heptaradical **3** under the same conditions. Two quasi-reversible redox pairs, which are more clearly separated at the lowest scan rate of 20 mV s^{-1}, can be observed, indicating that both the reduction states are reasonably stable. At higher scan rates, however, both the couples are partially overlapped. To determine accurately the standard potential and the relative intensity for both processes, the differential pulse voltammetry of heptaradical **3** was carried out. As is shown in Figure 6b, the voltammogram recorded at 20 mV s^{-1} displays two consecutive reduction peaks with peak potentials $E_p(R_1)$=−0.57 V vs SCE and $E_p(R_2)$=−0.76 V vs SCE and a relative intensity of 6–7:1. These peak potentials can be taken as the standard potentials for the first and second redox couples. The intensity ratio between both redox peaks is indicative of the contribution of six electrons in the first process and one electron in the second one. Therefore, the first peak is assigned to the reduction of the six external carbon-centered radicals and the second one to the internal trivalent carbon atom. Electrochemical analysis is a powerful tool in determining the extent of interactions between the electroactive groups in a molecule. The appearance of two redox couples suggests that the six trivalent carbon atoms in the periphery of the heptaradical **3** are electrochemically equivalent, each one being reduced at the same applied potential without any appreciable columbic charge interaction. A similar behavior should then be expected for the oxidation of heptaradical **3**. However, CV and DPV measurements recorded at the same scan rates revealed the existence of a quasi-reversible seven-electron redox process with $E°$=1.02 V vs SCE and with slight broadening of the oxidation and reduction peaks, associated to the equilibrium $\mathbf{3}-7e^- \rightleftharpoons \mathbf{3}^{7+}$. In this case, each trivalent carbon atom of the molecule is oxidized at essentially the same potential.

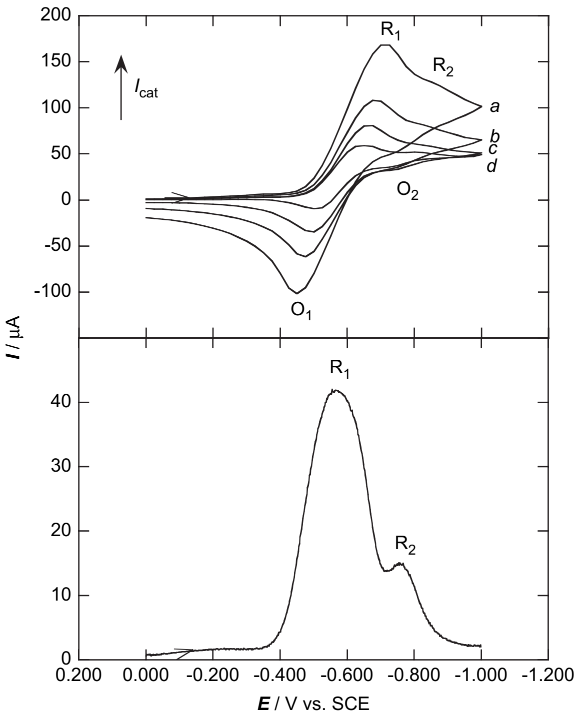


Figure 6. Up: cyclic voltammograms corresponding to the reduction of **3** (10^{-3} M) in CH_2Cl_2 with TBAP (0.1 M) on Pt at 25 °C. Initial and final potential 0 V; reversal potential −1.000 V; scan rate: (a) 200, (b) 100, (c) 50, (d) 20 mV s^{-1}. Down: differential pulse voltammogram for the reduction of **3** under the same conditions. Initial potential 0 V; final potential −1.000 V; scan rate 20 mV s^{-1}.

2.5. Thermal analysis

Thermogravimetric analysis (TGA) of heptaradical **3** and hexaradical **4** (both samples dried before analysis under vacuum and heated at 150 °C to remove solvent molecules) showed a stability in nitrogen at temperatures up to 300 °C (Fig. 7). Above this temperature a loss of weight (∼10−12 %) occurs, corresponding to the liberation of approximately 12 chlorines. This result was corroborated by elemental analysis of the product obtained after thermolysis of heptaradical **3** at 300 °C, which fitted quite well to the formula $C_{139}H_{42}Cl_{45}N_6O_6$ (molecular structure of **3** with 12 chlorines lost). Regardless of the different electronic structure of the core carbon atom, thermal diagrams of **3** and **4** are very similar, suggesting that dechlorination processes should correspond most probably to the external triphenylmethyl parts. Therefore, a sixfold cyclodechlorination of the six pairs of phenyls can take place to yield a macromolecule with six fluorenyl systems. Loss of chlorine atoms in both polyradicals is also confirmed by mass spectrometry

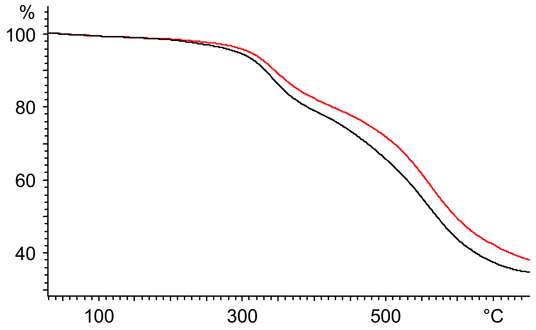


Figure 7. Thermogravimetric analysis of the heptaradical **3** (red line) and hexaradical **4** (black line). Initial and final temperatures: 30.0–700.0 °C; scan rate: 10.0 °C/min; nitrogen flow: 200.0 mL/min.

(MALDI/TOF). A high number of peaks corresponding to the loss of up to 10 chlorines appeared in the region of the molecular peak, those with an even number of chlorines being less intense. Further work to confirm the structure of dechlorinated structure is now in progress.

3. Conclusion

Radical TTM (**1**) has been easily functionalized in *meta* positions with six chlorocarbonyl substituents enabling the condensation with the amino function of radical **2**. Thus, polyradicals **3** and **4**, composed by radicals of the TTM series connected by amide bonds, have been prepared in good yields. This synthetic strategy avoids the generation of radical centers, always difficult, in the last stage of the sequential preparation, yielding **3** and **4** with very good agreement between magnetic susceptibility measurements and the expected values for 6 and 7 spin radicals, respectively. Analysis of the EPR spectra of them and of those of different biradical models, suggests the presence of strong electron–electron exchange and weak dipolar couplings. Macromolecules **3** and **4** are very stable polyradicals that are both cathodically reduced and anodically oxidized in electrochemical processes having an intense coloration in the three different redox states. Polyradical **3** is reduced in a seven-electron two-stage processes and oxidized in a seven-electron one-stage process.

4. Experimental

4.1. General procedures

Melting points were obtained by using a Köfler microscope 'Reichert' and are uncorrected. The IR spectra were recorded with a FTIR 'Bomem–Michalson' model MB-120 spectrophotometer. ^{1}H NMR spectra were determined at 200 MHz with Varian Gemini 200HC spectrometer. The electronic spectra were recorded with a Varian model Cary 300 Bio spectrophotometer. $CHCl_3$, CCl_4, and CH_2Cl_2 were dried over calcium chloride and distilled. THF was dried over sodium and distilled before use. High-resolution mass spectra were recorded with a VG Auto Spec 'Micromass Ins.' and matrix-assisted laser-desorption ionization/time-of-flight (MALDI/TOF) mass spectra were recorded using 2,5-dihydroxybenzoic acid or dithranol as a matrix. EPR spectra were recorded with a Varian E-109 spectrometer working in the X band and using a Varian E-257 temperature-controller to obtain spectra at temperatures as low as 130 K. A Bruker ESP 300 spectrometer with a Bruker ER 4112 HV continuous-flow liquid helium cryostat and an Oxford Instruments temperature-controller system was used to obtain EPR spectra at lower temperatures (4 K). Samples of polyradicals in CH_2Cl_2 or 2-methyltetrahydrofuran were introduced in quartz EPR tubes and degassed before being inserted into the EPR cavity. Handling of radicals in solution was performed in the dark. Magnetic susceptibility data for microcrystalline samples of polyradicals were measured from 1.8 to 300 K with a SQUID magnetometer operating with the field strength of 50 kOe. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out in a standard thermostated three-electrode cell. A platinum (Pt) disk with 0.093 cm^2 area was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a saturated calomel electrode (SCE), submerged in a salt bridge of the same electrolyte, which was separated from the test solution by a Vycor membrane. Solutions of monoradicals and polyradicals ($\sim 10^{-3}$ M) in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate as background electrolyte were studied by CV and DPV. The volume of all test solutions was 50 mL. Electrochemical measurements were performed under an Ar atmosphere and at 25 °C using an Eco Chemie Autolab PGSTAT100 potentiostat–galvanostat controlled by a computer with GPES software. Cyclic voltammograms of all solutions were recorded at scan rates (v) ranging from 20 to 200 mV s^{-1}, while their differential pulse voltammograms were obtained at 20 mV s^{-1}.

4.1.1. Tris(3,5-diformyl-2,4,6-trichlorophenyl)methane (9). A solution of tris(α,α,α',α',2,4,6-heptachloroxylyl)methane[6] (2.30 g) in fuming sulfuric acid (30 %, 50 mL) was heated (95 °C, 5 h). The resulting mixture was poured into cracked ice/water, and the precipitate was filtered, washed with water, and dried. The solid was treated with chloroform at reflux for 2 h, the solution was evaporated and the residue flash chromatographed (silica gel, CH_2Cl_2) to afford **9** (0.4 g, 25 %), mp 260–263 °C. ^{1}H NMR ($CDCl_3$) δ 10.32 (d, 6H), 7.68 (s, 1H); IR (KBr) 3397 (w), 2873 (w), 1712 (s), 1537 (s), 1350 (m), 1270 (w), 1217 (w), 1119 (w), 1040 (s), 994 (s), 970 (s), 816 (m), 735 (w), 703 (w) cm^{-1}; HRMS (*m/z*) for $C_{25}H_7Cl_9O_6$ (M^+): calcd 721.738037, found 721.739964.

4.1.2. Tris(3,5-dicarboxy-2,4,6-trichlorophenyl)methane (10). Sulfuric acid (7 mL) was added to a solution of **9** (0.096 g, 0.1 mmol) in acetone (18 mL) and, then, a solution of chromium(VI) oxide (0.1 g, 1 mmol) in water (5 mL) was slowly added. The mixture was stirred at room temperature (4 h) and volatile parts were evaporated. The residue in ethyl acetate was washed with water, dried over sodium sulfate and evaporated, yielding **10** (0.124 g, quantitative yield). IR (KBr): 3550–2100 (s), 1723 (s), 1620 (m), 1548 (s), 1400–1198 (m), 1116 (w), 1017 (w), 926 (w), 809 (w), 713 (w) cm^{-1}; HRMS (*m/z*) for $C_{25}H_7Cl_9O_{12}$ (M^+): cacld 817.707525, found 817.708077.

4.1.3. Tris(3,5-dichloroformil-2,4,6-trichlorophenyl)methane (6). A solution of **10** (0.065 g) in $SOCl_2$ (3 mL) was refluxed (22 h) and poured into water. The mixture was treated with an excess of sodium hydrogen carbonate and extracted with chloroform. The organic solution was washed with water, dried over sodium sulfate, and the solvent was evaporated. The residue was flash chromatographed (silica gel, hexane/$CHCl_3$ 3:1), to give **6** (0.046 g, 62 %), mp 300 °C (dec). IR (KBr): 3540 (w), 2924 (w), 1779 (s), 1547 (s), 1374 (m), 1282 (w), 1220 (m), 1138 (m), 1095 (s), 1014 (s), 945 (m), 836 (s), 813 (m), 794 (m), 735 (w), 724 (w), 701 (w) cm^{-1}; HRMS (*m/z*) for $C_{25}H_1Cl_{15}O_6$ (M^+): calcd 927.501254, found 927.503006.

4.1.4. Tris(3,5-dichloroformil-2,4,6-trichlorophenyl)methyl radical (5). An excess of aqueous solution of tetrabutylammonium hydroxide (1.5 M, 1.2 mL) was added to a solution of 6 (0.500 g, 0.53 mmol) in acetone (85 mL) and the mixture was stirred at room temperature (0.5 h). Then crushed chromium(VI) oxide (0.540 g) was added and the mixture was stirred (0.5 h) again. Acetone was eliminated at low pressure and the residue in chloroform, washed with aqueous solution of hydrochloric acid and water, was dried to give radical **5** (0.495 g, 98 %), mp 280–282 °C. IR (KBr): 1781 (s), 1525 (s), 1355 (m), 1107 (s), 1016 (s), 953 (w), 844 (s), 816 (m), 803 (m), 738 (w), 705 (w) cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$) 384 (22,900), 510 (575), 555 (600) nm; HRMS (*m/z*) for $C_{25}Cl_{15}O_6$ (M^+): calcd 928.490478, found 928.492935.

4.1.5. Heptaradical 3. A mixture of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (0.370 g, 0.69 mmol), radical **5** (0.101 g, 0.11 mmol) and cesium carbonate (0.378 g) in benzene (10 mL) was stirred at reflux (4 h) under an argon atmosphere. The solution was dried and the residue in chloroform was washed with HCl aqueous solution, dried over sodium sulfate, and evaporated. The residue was flash chromatographed (silica gel, hexane/$CHCl_3$ 1:4) to afford heptaradical **3** (0.357 g, 84 %), mp >320 °C (dec). IR (KBr): 3387 (w), 3294 (w), 3067 (w), 2928 (w), 1702 (m), 1678 (m), 1574 (s), 1553 (s), 1491 (m), 1373 (s), 1300 (m), 1236 (w), 1209 (w), 1182 (m), 1138 (m), 1084 (w), 951 (w), 927 (w), 858 (s), 810 (s), 796 (s) cm^{-1}. Anal. Calcd for $C_{139}H_{42}Cl_{57}N_6O_6$: C, 42.7; H, 1.1; N, 2.1; Cl, 51.6. Found: C, 42.7; H, 1.2; N, 2.1; Cl, 51.6; MS (MALDI/TOF) (*m/z*) for $C_{139}H_{42}Cl_{57}N_6O_6$ (M^+): calcd 3912.38, found: 3914.80

4.1.6. Hexaradical 4. A mixture of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (0.372 g, 0.69 mmol), methane **6** (0.102 g, 0.11 mmol) and cesium carbonate (0.380 g) in benzene (10 mL) was stirred at reflux (36 h) under an argon atmosphere. The reaction mixture was dried and the residue in chloroform washed with HCl aqueous solution, was dried over sodium sulfate, and evaporated. The residue was flash chromatographed (silica gel, $CHCl_3$) to afford hexaradical **4** (0.123 mg, 29 %), mp >313 °C (dec). IR (KBr): 3650 (w), 3389 (w), 3071 (w), 1684 (m), 1576 (s), 1557 (s), 1526 (m), 1494 (m), 1374 (s), 1293 (m), 1234 (w), 1184 (m), 1133 (w), 1082 (w), 948 (w), 925 (w), 857 (s), 811 (s), 796 (s) cm^{-1}; MS (MALDI/TOF) (*m/z*) for $C_{139}H_{42}Cl_{57}N_6O_6$ (M^+): calcd 3913.38, found 3914.77.

4.1.7. Biradical 11. A solution of radical **2** (0.063 g, 0.12 mmol) in benzene (20 mL) was added dropwise to a mixture of radical **14** (0.100 g, 0.11 mmol), sodium hydrogen carbonate (0.200 g) and benzene (20 mL) and then stirred at reflux (9.5 h) under an argon atmosphere. The reaction mixture was dried and the residue in chloroform washed with HCl aqueous solution, was dried over sodium sulfate, and evaporated. The residue was flash chromatographed (silica gel, hexane/$CHCl_3$ 1:1) to give recovered radical **14** (0.046 g) and biradical **11** (0.061 g, 80 %), mp >250 °C (dec). IR (KBr): 3397 (w), 3140 (w), 3072 (w), 1780 (m), 1703 (m), 1683 (m), 1672 (m), 1571 (s), 1560 (s), 1525 (s), 1498 (m), 1434 (w), 1374 (m), 1334 (m), 1261 (m), 1224 (w), 1180 (m), 1137 (m), 1126 (m), 1068 (m), 1029 (w), 989 (m), 950 (m), 912 (w), 858 (s), 806 (s), 757 (s), 715 (w) cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$) 385 (49,600), 555 (1800) nm; MS (MALDI/TOF) (*m/z*) for $C_{40}H_7Cl_{22}NO_2$ (M^+): calcd 1312.30, found: 1312.30.

4.1.8. Biradical 12. A mixture of radical **5** (117 mg, 0.12 mmol), radical **2** (0.072 g, 0.13 mmol), cesium carbonate (122 mg) and benzene (10 mL) was stirred at reflux in an inert atmosphere (4 h). The reaction mixture was dried and the residue in chloroform washed with HCl aqueous solution, was dried over sodium sulfate, and evaporated. The residue was flash chromatographed (silica gel, hexane/$CHCl_3$ 1:1) to give biradical **12** (0.067 g, 37 %), mp >300 °C (dec). IR (KBr): 3385 (w), 3119 (w), 3063 (w), 1783 (s), 1702 (m), 1571 (s), 1551 (s), 1526 (s), 1371 (m), 1298 (w), 1183 (m), 1138 (m), 1049 (s), 1015 (s), 858 (m), 806 (s) cm^{-1}; MS (MALDI/TOF) (*m/z*) for $C_{44}H_7Cl_{22}NO_6$ (M^+): calcd 1425.40, found: 1425.43.

4.1.9. Biradical 13. A mixture of 2,4,5,6-tetrachloroisophthaloyl dichloride (100 mg, 0.29 mmol), radical **2** radical (315 mg, 0.59 mmol), sodium bicarbonate (250 mg), and benzene (5 mL) was stirred at reflux in an inert atmosphere (48 h). The benzene was distilled off and the residue was treated with chloroform/water. The insoluble fraction, separated by filtration, was characterized as biradical **13** (0.123 g, 31 %), mp=374 °C (dec). IR (KBr): 3397 (w), 3237 (w), 3142 (w), 3068 (w), 1663 (s), 1578 (s), 1555 (s), 1525 (m), 1498 (m), 1383 (s), 1370 (s), 1300 (m), 1238 (w), 1182 (m), 1136 (m), 1083 (w), 950 (w), 924 (w), 857 (s), 809 (s), 794 (s), 758 (w), 723 (w) cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$) 377 (60,500), 510 (2030), 554 (1980) nm; MS (MALDI/TOF) (*m/z*) for $C_{139}H_{42}Cl_{57}N_6O_6$ (M^+): calcd 1335.57, found: 1335.60.

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