JOC *Article*

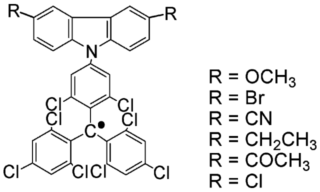
Red Organic Light-Emitting Radical Adducts of Carbazole and Tris(2,4,6-trichlorotriphenyl)methyl Radical That Exhibit High Thermal Stability and Electrochemical Amphotericity

Dolores Velasco,[†] Sonia Castellanos,[‡] Marc López,[‡] Francisco López-Calahorra,[†]
Enric Brillas,[§] and Luis Juliá*,[‡]

Departament de Química Orgànica, Institut de Nanociències I Nanotecnologia, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain, Departament de Química Orgànica Biològica, Institut d'Investigacions Químiques i Ambientals (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain, and Departament de Química Física, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

ljbmoh@cid.csic.es

Received April 27, 2007



Synthesis and characterization of new carbazolyl derivatives with a pendant stable radical of the TTM (tris-2,4,6-trichlorophenylmethyl radical) series are reported. The EPR spectra, electrochemical properties, absorption spectra, and luminescent properties of these radical adducts have been studied. All of them show electrochemical amphotericity being reduced and oxidized to their corresponding stable charged species. The luminescence properties of them cover the red spectral band of the emission. The luminescence of the electron-rich carbazole adducts shows the donor−acceptor nature of the excited state. On the other hand, the EPR parameters of these radical adducts show an imperceptible variation with the substituents in the carbazole.

Introduction

Carbazole is a heterocycle with the nitrogen atom singly bonded to carbon atoms, and the low-lying n → π^* transitions in the electronic spectrum involving the nonbonding electrons on nitrogen have properties similar to those of $\pi \rightarrow \pi^*$ transitions. This is why carbazole is a fundamental chromophore that gives an efficient emission at $\lambda \sim 340$ nm in dilute solutions.[1] The synthesis and applications of carbazole derivatives have been a source of great interest for chemists and materials scientists due to their intrinsic photophysical and redox properties. They exhibit relatively intense luminescence and high photoconductivities and undergo reversible oxidation processes making them suitable as hole carriers.[2] Consequently, carbazoles are widely used as building blocks for potential organic semiconductors.[3]

In the field of organic light-emitting diodes (OLED), carbazoles are used as the materials for hole-transporting and light-emitting layers.[4,5] Many carbazoles have a sufficiently high triplet energy to host red as full-color triplet emitters.[6] In

---

[†] Departament de Química Orgànica, Institut de Nanociéncies i Nanotecnologia, Universitat de Barcelona.

[‡] Institut d'Investgacions Químiques i Ambientals (CSIC).

[§] Departament de Química Física, Universitat de Barcelona.

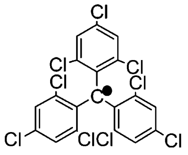
(1) Berlman, I. B. In *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971; p 205. Mastrangelo, J. C.; Conger, B. M.; Chen, S. H.; Bashir- Hashemi, A. *Chem. Mater.* **1997**, *9*, 227−232. Conger, B. M.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H. *J. Phys. Chem. A* **1998**, *102*, 9213−9218. Castex, M. C.; Olivero, C.; Pichler, G.; Ades, D.; Cloutet, E.; Siove, A. *Synth. Met.* **2001**, *122*, 59−61.

(2) Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297. Parimal, K.; Justin Thomas, K. R.; Jiann, T. L.; Tao, Y. T.; Chien, C. H. *Adv. Funct. Mater.* **2003**, *13*, 445−452. Akira, B.; Ken, O.; Wolfgang, K.; Rigoberto, C. A. *J. Phys. Chem. B* **2004**, *108*, 18949−18955.

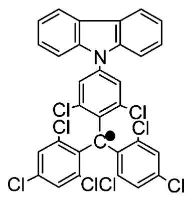
(3) Wakim, S.; Bouchard, J.; Simard, M.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4386−4388. Wakim, S.; Bouchard, J.; Bouchard, J.; Blouin, N.; Michaud, A.; Leclerc, M. *Org. Lett.* **2004**, *6*, 3413−3416. Martin, S.; Klaus, K.; Doris, H.; Peter, S.; Sepas, S.; Dago, D. L. *Chem. Mater.* **2005**, *17*, 3031−3039. Nicolas, D.; Jean, F. M.; Nicolas, L.; Salem, W.; Ye, T.; Mario, L. *Adv. Funct. Mater.* **2005**, *15*, 1671−1682. Morin, J. F.; Leclerc, M.; Ades, D.; Siove, A. *Macromol. Rapid Commun.* **2005**, *26*, 761−764.

10.1021/jo0708846 CCC: $37.00

addition, the carbazole ring is easily functionalized and covalently linked to other molecules.[7,8] However, the poor nucleophilic assistance of the nonbonding electron pair on the nitrogen has made difficult its incorporation into aromatic systems by classical methods, requiring severe reaction conditions. Several synthetic strategies to obtain *N*-aryl derivatives of carbazole by using Cu/bronze[9] or palladium catalyst[10] have been published. Thus, different *N*-arylcarbazoles have been prepared from electron-rich and electron-poor halobenzenes as precursors, mainly bromo- and iodobenzenes. This is an easy and direct way to successfully couple carbazole into polymers such as poly(*p*-bromostyrene).[11] The incorporation of carbazole in the main chain[12] or as a pendant group in the framework of many polymers[13] can greatly improve the photoconductivities and hole transporting properties of them. Finally, another important property of carbazole derivatives for technological applications is their high thermal and photochemical stabilities. Despite the huge amount of work already carried out with carbazoles, more research efforts are needed to design and synthesize new compounds with novel and improved properties to meet all the demands that applications require. Recently, we have reported the synthesis and properties of a new carbazole derivative, the (4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical ($\mathbf{1}^{\bullet}$), resulting from the coupling of the *N-H*-carbazole to the stable tris(2,4,6-trichlorophenyl)-methyl (TTM) radical. This new paramagnetic adduct has interesting electrochemical and luminescent properties and high thermal stability.[14] As far as we know, this is the third example of a stable radical anchored to carbazole. The first two reported examples refer to the preparation and characterization of *N*-picryl-9-aminocarbazolyl radical[15] and a diphenylpicryl-type diradical of a carbazole dimer.[16] Radicals of the series of TTM are a kind of organic carbon-centered free radicals showing great stability mainly due to steric hindrance of six chlorine atoms around the trivalent carbon.[17,18] All of these radicals are completely disassociated and very stable either in solid or in solution. Their inefficiency to abstract H-atoms from hydrogen-labile species is accounted for by steric hindrance, and therefore they are inoperatives in these processes. However, they are very sensitive to electron-transfer reactions, being easily reduced to carbanions with stabilities comparable to their precursors in the presence of electron donor species, so that their electrochemical behavior shows reversible reduction processes.



TTM



($\mathbf{1}^{\bullet}$)

Nitroxide radicals are known to be excellent fluorescent quenchers of aromatic hydrocarbons, presumably by an electron-

---

(4) Adamovich, V. I.; Cordero, S. R.; Djurovich, P. I.; Tamayo, A.; Thompson, M. E.; D'Andrade, B. W.; Forrest, S. R. *Org. Electron.* **2003**, *4*, 77−87. van Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stössel, P.; Brunner, K. *J. Am. Chem. Soc.* **2004**, *126*, 7718−7727. Morin, J. F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4619−4626. Justin Thomas, K. R.; Velusamy, M.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *Adv. Funct. Mater.* **2004**, *14*, 387−392. Brunner, K.; van Dijken, A. V.; Borner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035−6042.

(5) Morin, J. F.; Leclerc, M. *Macromolecules* **2002**, *35*, 8413−8417.

(6) Gruner, J.; Wittmann, H. F.; Hamer, P. J.; Friend, R. H.; Huber, J.; Scherf, U.; Mullen, K.; Moratti, S, C.; Holmes, A. B. *Synth. Met* **1994**, *67*, 181−185. Uekawa, M.; Miyamoto, Y.; Ikeda, H.; Kaifu, K.; Ichi, T.; Nakaya, T. *Thin Sol. Fims* **1999**, *352*, 185−188. Park, J. W.; Lee, J. H.; Lee, H. S.; Kang, D. Y.; Kim, T. W. *Thin Sol. Films* **2000**, *363*, 90−93. Ahan, K. W.; Liu, Y. Q.; Yu, G.; Wu, X.; Zhu, D. B.; Sun, R. G.; Wang, D. K.; Epstein, A. J. *J. Mater. Chem.* **2001**, *11*, 1606−1611. Walsh, C. J.; Sooksimuang, T.; Mandal, B. K. *J. Porph. Phthal.* **2001**, *5*, 803−805. Ko, C. W.; Tao, Y. T.; Lin, J. T.; Thomas, K. R. J. *Chem. Mater.* **2002**, *14*, 357−361. Thomas, K. R. J.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *J. Mater. Chem.* **2002**, *12*, 3516−3522. Lee, J. H.; Woo, H. S.; Kim, T. W.; Park, J. W. *Opt. Mater.* **2003**, *21*, 225−229. Das, R. R.; Lee, C. L.; Noh, Y. Y.; Kim, J. J. *Opt. Mater.* **2003**, *21*, 143−146. Kundu, P.; Thomas, K. R. J.; Lin, J. T.; Tao, Y. Y.; Chien, C. H. *Adv. Funct. Mater.* **2003**, *13*, 445−452. Suzuki, M.; Tokito, S.; Kamachi, M.; Shirane, K.; Sato, F. *J. Photopolym. Sci. Tech.* **2003**, *16*, 309−314. Anni, M.; Manna, L.; Cingolani, R.; Valerini, D.; Creti, A.; Lomascolo, M. *App. Phys. Lett.* **2004**, *85*, 4169−4171. Woo, H. S.; Cho, S.; Kwon, T. W.; Park, D. K.; Kim, Y. B.; Czerw, R.; Carroll, D. L.; Park, J. W. *J. Korean Phys. Soc.* **2005**, *46*, 981−984. Li, K. Z.; Zhang, Y.; Yang, R. Q.; Huang, J.; Yang, W.; Cao, Y. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 2325−2336.

(7) Zhang, Z. B.; Fujiki, M.; Tang, H. Z.; Motonaga, M.; Torimitsu, K. *Macromolecules* **2002**, *35*, 1988−1990. Brizius, G.; Kroth, S.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 5317−5319. Paik, K. L.; Baek, N. S.; Kim, H. K.; Lee, J-H.; Lee, Y. *Macromolecules* **2002**, *35*, 6782. Bouchard, J.; Belletele, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2003**, *36*, 4624−4630. Sanda, F.; Kawaguchi, T.; Masuda, T.; Kobayashi, N. *Macromolecules* **2003**, *36*, 2224−2229. Kim, K.; Hong, Y. R.; Lee, S. W.; Jin, J. I.; Park, Y.; Sohn, B. H.; Kim, W. H.; Park, J. K. *J. Mater. Chem.* **2001**, *11*, 3023−3030.

(8) Díaz, J. L.; Dobarro, A.; Villacampa, B.; Velasco, D. *Chem. Mater.* **2001**, *13*, 2528−2536. Díaz, J. L.; Villacampa, B.; López-Calahorra, F.; Velasco, D. *Chem. Mater.* **2002**, *14*, 2240−2251.

(9) Martinez-Palau, M.; Perea, E.; López-Calahorra, F.; Velasco, D. *Lett. Org. Chem.* **2004**, *1*, 231−237.

(10) Mann, G.; Hartwig, J. F.; Driver, M. S.; Fernández-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827−828. Watanabe, M.; Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **2000**, *41*, 481−483.

(11) Kanbara, T.; Yokokawa, Y.; Hasegawa, K. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 28−34.

(12) Zhang, Y.; Wada, T.; Sasabe, H. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 2289−2298. Wang, Q.; Gharvi, A.; Li, W.; Yu, L. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1997**, *38*, 516. Morin, J. F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680−4682. Huang, J.; Niu, Y.; Yang, W.; Mo, Y.; Yuan, M.; Cao, Y. *Macromolecules* **2002**, *35*, 6080−6082. Jiang, J.; Jiang, C.; Yang, W.; Zhen, H.; Hung, F.; Cao, Y. *Macromolecules* **2005**, *38*, 4072−4080.

(13) Gratt, J.; Cohen, R. E. *Macromolecules* **1997**, *30*, 3137−3140. Mustonen, I.; Hukka, T.; Pakkanen, T. *Macromol. Rapid Commun.* **2000**, *21*, 1286−1290. Hwang, J.; Sohn, J.; Park, S. Y. *Macromolecules* **2003**, *36*, 7970−7976. Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297−1353 and references cited therein. Hsiao, S. H.; Chen, C. W.; Liou, G. S. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3302−3313. Chen, Z.; Liu, Y.; Zhang, C.; Bai, F. *J. Appl. Polym. Sci.* **2004**, *92*, 2777. Liang, F.; Kurata, T.; Nishide, H.; Kido, J. *J. Polym. Sci. Part A Polim. Chem.* **2005**, *43*, 5765−5773.

(14) Gamero, V.; Velasco, D.; Latorre, S.; López-Calahorra, F.; Brillas, E.; Juliá, L. *Tetrahedron Lett.* **2006**, *47*, 2305−2309.

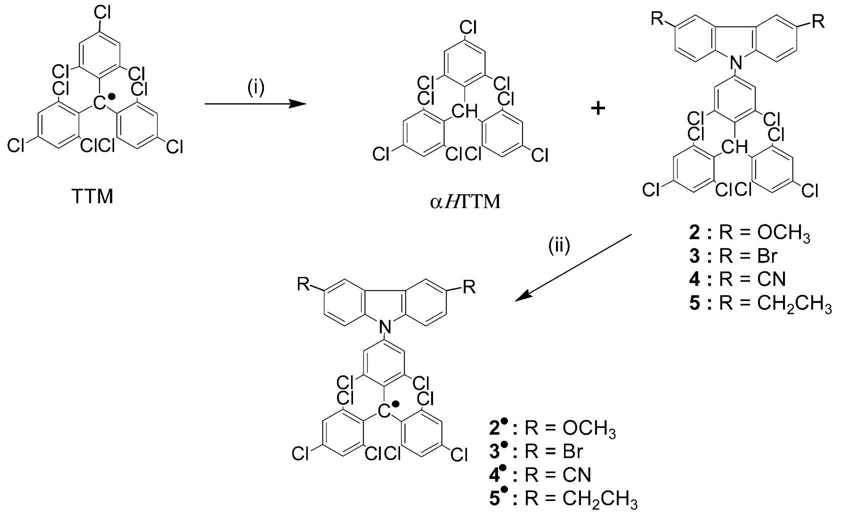
(15) Kikuchi, C.; Cohen, V. W. *Phys. Rev.* **1954**, *93*, 394−399. Jarrett, H. S. *J. Chem. Phys.* **1953**, *21*, 761. Lord, N. W.; Blinder, S. M. *J. Chem. Phys.* **1961**, *34*, 1693−1708. Makino, H.; Nishiguchi, H.; Deguchi, Y.; Takaki, H. *Tetrahedron Lett.* **1968**, 2267−2269.

(16) Kozaki, M.; Okada, K. *Synth. Met.* **2001**, *119*, 177−178.

(17) Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravitlles, C.; Olivella, S.; Brichfeus, J. *J. Phys. Chem.* **1987**, *91*, 5608−5616.

(18) Carilla, J.; Fajarí, L. l.; Juliá, L.; Riera, J.; Viadel, L. l. *Tetrahedron Lett.* **1994**, *35*, 6529−6532. Teruel, L.; Viadel, L. l.; Carilla, J.; Fajarí, L. l.; Brillas, E.; Sañé, J.; Rius, J.; Juliá, L. *J. Org. Chem.* **1996**, *61*, 6063−6066. Carilla, J.; Fajarí, L. l.; Juliá, L.; Sañé, J.; Rius, J. *Tetrahedron* **1996**, *52*, 7013−7024. Viadel, L. l.; Carilla, J.; Brillas, E.; Labarta, A.; Juliá, L. *J. Mater. Chem.* **1998**, *8*, 1165−1172. Domingo, V. M.; Burdons, X.; Brillas, E.; Carilla, J.; Rius, J.; Torrelles, X.; Juliá, L. *J. Org. Chem.* **2000**, *65*, 6847−6855. Carriedo, G. A.; García Alonso, F. J.; Gómez Elipe, P.; Brillas, E.; Juliá, L. *Org. Lett.* **2001**, *3*, 1625−1628. Torres, J. L.; Varela, B.; Brillas, E.; Juliá, L. *J. Chem. Soc., Chem. Commun.* **2003**, 74−75. Gabino, G. A.; García Alonso, F. J.; Gómez Elipe, P.; Brillas, E.; Labarta, A.; Juliá, L. *J. Org. Chem.* **2004**, *69*, 99−104. Jiménez, A.; Selga, A.; Torres, J. L.; Juliá, L. *Org. Lett.* **2004**, *6*, 4583−4586.

SCHEME 1[a]



[a] Reagents: (i) 3,6-disubstituted carbazole, Cs_2CO_3, DMF; (ii) NaOH, Et_2O/DMSO and then I_2 for **2** and **3**, NaOH, Et_2O/DMSO and then 2,3-dicyano-4,5-dichloroquinone for **4** or Bu_4NOH, THF, and then tetrachloro-*p*-quinone for **5**.

exchange interaction between the nitroxide doublet ground state and the excited singlet state of the fluorophore.[19] For this reason, many nitroxide−fluorophore adducts are applied as optical sensors of radicals and redox reactions.[20] However, radical adduct **1•** shows good luminescent properties with efficiencies approximately as high as those of the parent *N-H*-carbazole and emission wavelengths dramatically shifted to the red region (for instance, $\lambda = 334/350$ nm for *N-H*-carbazole and $\lambda = 628$ nm for **1•** in cyclohexane). The different behavior of **1•** with regard to the nitroxide radicals is that the fluorophore group in **1•** is a doublet-excited-state as the trivalent carbon atom is being part of the chromophore. The preparation of the reported adduct **1•** has allowed assembly in one species of the redox properties and paramagnetic character of the TTM radical and the luminescent and hole-conductivity properties of the carbazole in view of their potential applications as chemosensor of redox processes and/or light-emitting diodes (LEDs). Reduction of the adduct **1•** leads to the formation of a diamagnetic product insensitive to the electron paramagnetic resonance (EPR) spectroscopy and resulting in a shift from the red to the blue region in the luminescence emission (the wavelength of the emission of the diamagnetic product is practically the same value of the *N-H*-carbazole). Furthermore, stable organic radicals are intensively investigated due to particular features induced by the presence of an unpaired electron. As part of our research in these multifunctional species, we have focused our efforts in the preparation of new entities derived from radical adduct **1•** to modulate their redox and optical properties by simply introducing electron donors and electron acceptors into the carbazole subunit. Here, we report on the synthesis, absorption spectra, luminescence properties, redox behavior, and EPR spectra of novel stable free radical adducts **2•**−**6•**, and the preparation, absorption spectra and luminescent properties of their diamagnetic precursors **2**−**6** as model compounds.

Results and Discussion

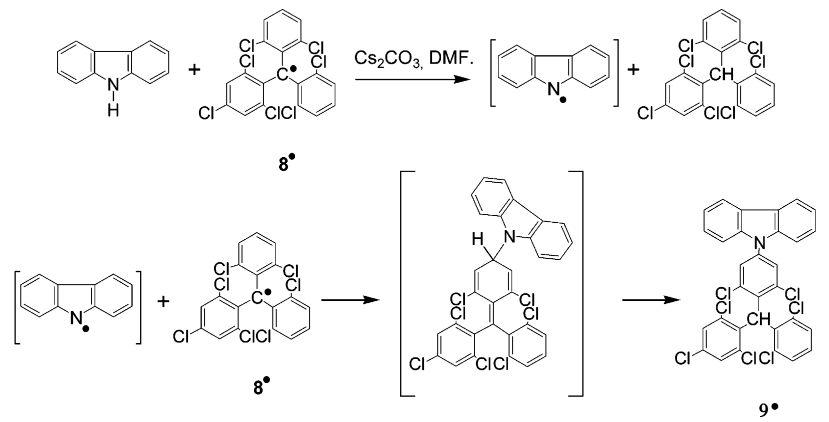
Synthesis. The experimental methods to prepare the radical adducts **2•**−**7•** of the TTM series are displayed in three different schemes. Scheme 1 shows the synthesis of radical adducts **2•**−**5•** following the classical method carried out to prepare the parent adduct **1•**. Therefore, the TTM radical with an excess of the 3,6-disubstituted carbazole in the presence of the appropriate base, cesium carbonate, in boiling dimethylformamide as solvent, followed by hydrolysis with an excess of diluted hydrochloric acid gave a mixture of the corresponding carbazolyltriphenylmethane (α*H*carbazolyl-TTM), with moderate yield, and α*H*TTM. Next, α*H*carbazolyl-TTMs **2**−**4** in dimethylsulfoxide/diethyl ether with sodium hydroxide and then with iodine or 2,3-dicyano-4,5-dichloroquinone and α*H*carbazolyl-TTM **5** in tetrahydrofuran with an aqueous solution of tetrabutylammonium hydroxide (TBAH) followed by oxidation with 2,3,5,6-tetrachloro-*p*-benzoquinone rendered pure adducts **2•**−**5•** as nicely colored crystalline solids which are stable in solid melting at high temperatures with decomposition (see the Experimental Section). This is an interesting coupling reaction between the carbazole nitrogen and a *p*-carbon atom of the TTM radical with the substitution of a chlorine atom. The presence of α*H*TTM as a byproduct in all these experiments suggests that some sort of radical mechanism is operative in these reactions. Consequently, it seems that the carbazole molecule in basic medium is oxidized to the N-carbazolyl radical by electron transfer to TTM to form α*H*TTM after hydrolysis, and then the carbazolyl radical couples with another TTM to give the diamagnetic species α*H*carbazolylTTM after further reduction with more carbazole. This mechanism has been confirmed by two experimental tests: (1) α*H*TTM does not react with carbazole in the same conditions, and (2) the coupling reaction of carbazole with bis(2,6-dichlorophenyl)(2,4,6-trichlorophenyl)-methyl radical (**8•**), which shows two free para positions, yields besides the α*H*TTM as byproduct the α*H*carbazolylTTM **9** as

---

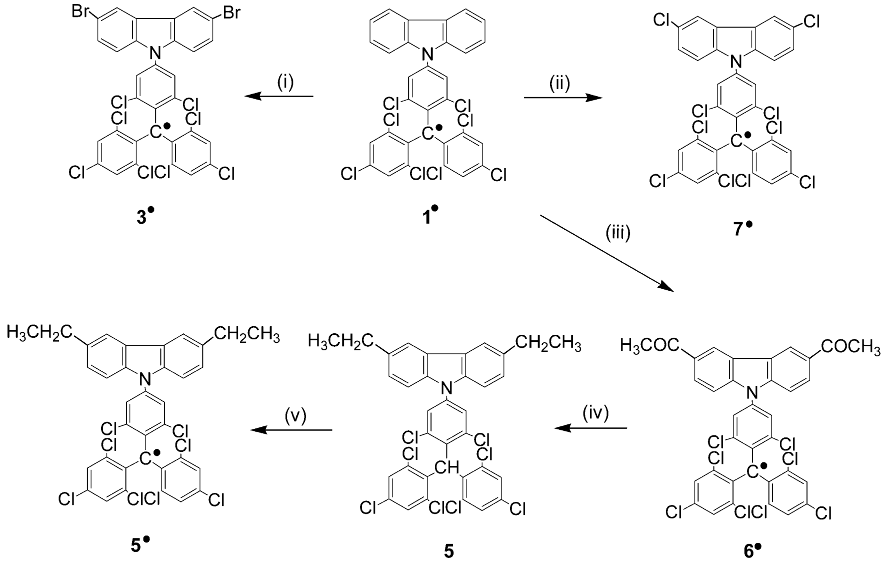
[19] Green, J. A.; Singer, L. A.; Parks, J. H. *J. Chem. Phys.* **1973**, *58*, 2690−2695. Green, J. A.; Singer, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 2730−2733. Watkins, A. R. *Chem. Phys. Lett.* **1974**, *29*, 526−528. Kuzmin, V. A.; Tatikolov, A. S. *Chem. Phys. Lett.* **1977**, *51*, 45−47. Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 6205−6210. London, E. *Mol. Cell. Biochem.* **1982**, *45*, 181−188. Atik, S. S.; Singer, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 3234−3235. Scaiano, J. C.; Paraskevopoulos, C. I. *Can. J. Chem.* **1984**, *62*, 2351−2354.

[20] Blough, N. V.; Simpson, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 1915−1917. Herbelin, S. E.; Blough, *J. Phys. Chem. B* **1998**, *102*, 8170−8176. Lozinsky, E. N. V.; Martin, V. V.; Berezina, T. A.; Shames, A. I.; Weis, A. L.; Likhtenshtein, G. I. *J. Biochem. Biophys. Methods* **1999**, *38*, 29−42. Ziessel, R.; Stroh, C. *Org. Lett.* **2003**, *5*, 2397−2400.

SCHEME 2

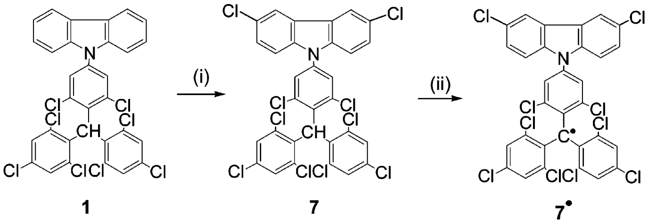


SCHEME 3[a]



[a] Reagents: (i) *N*-bromosuccinimide, silica gel, CH_2Cl_2; (ii) SO_2Cl_2, CH_2Cl_2; (iii) CH_3COCl, $AlCl_3$, CS_2; (iv) Zn, $HgCl_2$, HCl, toluene; (v) Bu_4NOH, THF, and then tetrachloro-*p*-quinone.

SCHEME 4[a]



[a] Reagents: (i) SO_2Cl_2, CH_2Cl_2; (ii) Bu_4NOH, THF, and then tetrachloro-*p*-quinone.

a result of the substitution of one *p*-hydrogen by the carbazole nitrogen and not the *p*-chlorine of the other phenyl substituent. The suggested mechanism is shown in the Scheme 2. In the first step, the electron transfer gives most probably the corresponding anion **8**$^-$ that is then protonated to **8**. The second step presents a simple coupling between two radicals with further rearrangement to adduct **9**$^\bullet$.[21]

Direct bromination of adduct **1**$^\bullet$ with *N*-bromosuccinimide in CH_2Cl_2 in the presence of silica gel gives dibromocarbazolylTTM radical **3**$^\bullet$. A Friedel−Crafts reaction on adduct **1**$^\bullet$ with acetyl chloride in carbon disulfide in the presence of $AlCl_3$ leads to adduct **6**$^\bullet$. Both radical adducts **3**$^\bullet$ and **6**$^\bullet$ are obtained in excellent yields. DichlorocarbazolylTTM radical **7**$^\bullet$ is obtained with moderate yield by treatment of adduct **1**$^\bullet$ with sulfuryl chloride in CH_2Cl_2. These new radicals are prepared by substitution reactions on the carbazolyl moiety of **1**$^\bullet$ without impairment of the radical character of the molecule. Reduction of the carbonyl groups of **6**$^\bullet$ with an amalgam of Zn−Hg gives the triphenylmethane **5**. In this reaction, besides the reduction of the carbonyl group by a Clemmensen reaction, the trivalent carbon atom is also reduced to form the diamagnetic compound **5**. Treatment of **5** with an aqueous solution of TBAH and then with tetrachloro-1,4-benzoquinone yields adduct **5**$^\bullet$ (Scheme 3). Chlorination of α*H*TTM with sulfuryl chloride in CH_2Cl_2 gives an excellent yield of the triphenylmethane **7** which yields adduct **7**$^\bullet$ by neutralization with TBAH and then oxidation with tetrachloro-1,4-benzoquinone (Scheme 4).

All these radical adducts **2**$^\bullet$−**7**$^\bullet$ are colored crystalline solids with high thermal stability (they show high melting points by DSC analysis without decomposition; they start to decompose when they melt; see Experimental section and Figures S19−S24, Supporting Information), and have been fully characterized.

---

(21) Castellanos, S.; López, M.; Juliá, L. Unpublished results.

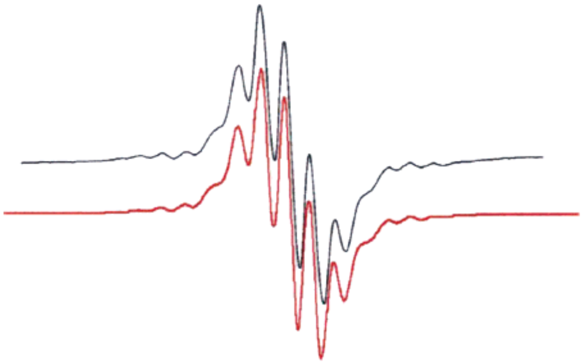


FIGURE 1. EPR spectrum of radical adduct **6**$^\bullet$: (black) **6**$^\bullet$ in CH_2Cl_2 solution at 174 K; (red) computer simulation.

TABLE 1. ***g* Values and Hyperfine Coupling Constants in Gauss for Radical Adducts 1$^\bullet$−7$^\bullet$ in CH_2Cl_2 ($\sim 10^{-3}$ M)^a**

adduct	g^b	1H	$^{13}C(\alpha)^c$	$^{13}C(arom)^c$	H_{pp}
1$^{\bullet d}$	2.0032	1.20	28.9	10.70	0.60
2$^\bullet$	2.0031	1.20	28.3	10.70	0.60
3$^\bullet$	2.0032	1.23	26.0	10.65	0.66
4$^\bullet$	2.0034	1.28	27.5	10.55	0.68
5$^\bullet$	2.0033	1.20	27.9	10.50	0.65
6$^\bullet$	2.0032	1.20	27.9	10.50	0.65
7$^\bullet$	2.0034	1.25	28.8	10.50	0.65

^{a} The hfc constants for six 1H in meta and ^{13}C(arom) (adjacent to α-carbon) and values for ΔH_{pp} (peak to peak line width) are determined at 160 ± 5 K and checked by computer simulation. ^{b} *g* values are measured against dpph (2.0037 ± 0.0002) at 298 K. ^{c} Natural abundance of ^{13}C isotope: 1.10%. ^{d} Taken from ref 14.

Electron Paramagnetic Resonance. X-band EPR spectra of the carbazolyl-TTM radical adducts **2**$^\bullet$−**7**$^\bullet$ are recorded in CH_2Cl_2 solution ($\sim 10^{-3}$−10^{-4} M) at 298 ± 3 K and 160 ± 15 K, and their spectral data are reported in Table 1 together with the data for adduct **1**$^\bullet$. In all cases, *g* values are similar and very close to that of the TTM radical ($g = 2.0034 \pm 0.0002$) and of the free electron ($g_e = 2.0023$), in agreement with the expected small spin−orbit interaction. All of the spectra at room temperature consisted of a broad and single line, along with a small equidistant pair of lines in both sides of the main spectrum. This small pair corresponds to the strong coupling of the free electron with the α-^{13}C nucleus, and its values are listed in Table 1. At low temperature, the spectra showed an overlapped multiplet of very close 7 lines corresponding to the weak coupling with the six equivalent aromatic hydrogens in the meta positions, and two weak multiplets in both sides of the central multiplet attributed to the coupling with the three bridgehead-^{13}C nuclei adjacents to the α-carbon atom. Values for all of these couplings are also reported in Table 1. As an example, Figure 1 shows the spectrum of the adduct **6**$^\bullet$ in CH_2Cl_2 solution at 174 K (EPR spectra of radical adducts **2**$^\bullet$−**5**$^\bullet$ and **7**$^\bullet$ are collected in Figures S13−S18, Supporting Information).

Two important points come from an analysis of data given in Table 1. First, relatively large values of the coupling of the free electron with α and bridgehead ^{13}C atoms, small values with the *m*-hydrogens, and no appreciable values with the carbazolyl ring can be observed. Second, all of the radicals show spectral parameters very similar irrespective of the different electron-donor and electron-withdrawing substituents in the carbazolyl ring. Moreover, all of the parameters displayed in Table 1 are also very similar to those of TTM radical, independent of the substitution of a *p*-chlorine atom by the carbazolyl ring. These results suggest that the distribution of the semioccupied molecular orbital (SOMO) in these molecules is localized mainly around the central carbon atom and is not influenced by the carbazolyl ring. In fact, X-ray analysis of the molecular structure of TTM radical indicated that the phenyl rings are twisted around their bonds with the central carbon atom (angles about 48°) due to the presence of six chlorine atoms in the ortho position, adopting a propeller-like conformation.[17]

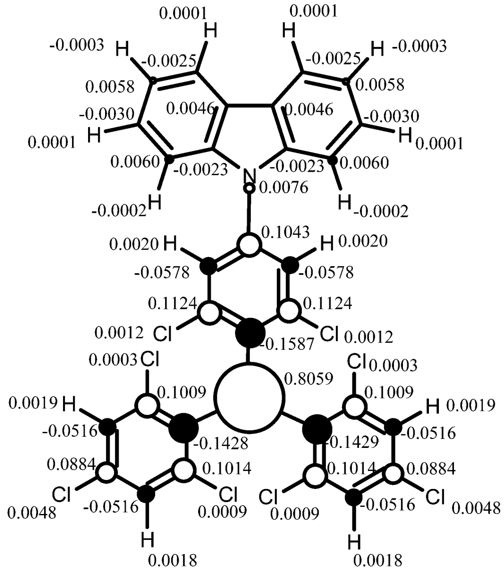


FIGURE 2. Total atomic spin densities of radical **1**$^\bullet$.

To discuss the coupling constants of the free electron with the *m*-hydrogens and with the ^{13}C nuclei in detail, the DFT calculations of the geometry and spin density distribution for adduct **1**$^\bullet$ were performed by the UB3LYP/6-31G method. Dihedral angles between phenyl groups and the plane defined by the central sp^2-carbon atom, 45.7° 48.5°, and 48.9°, are in good agreement with those observed for the molecular structure of the TTM radical (48.1°, 47.1°, and 48.1°) by X-ray crystallographic analysis. In addition, the carbazolyl ring is also twisted an angle of −48.1° around its N−C bond with the phenyl ring. The total atomic spin densities are illustrated in Figure2. The spin density resides mainly on the trivalent carbon atom since the out-of-plane torsions of the phenyl rings make the free electron be poorly delocalized on them and the spin density has practically no appreciable value on the carbazolyl ring.

Electrochemical Studies. Cyclic voltammetry (CV) is used to investigate the redox potentials of these new carbazolyl-TTM radical adducts **2**$^\bullet$−**7**$^\bullet$ to know their electrochemical properties and their electronic structure. Cyclic voltammograms were recorded in CH_2Cl_2 solution ($\sim 10^{-3}$ M) containing tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte on a platinum disk as working electrode using a saturated calomel electrode (SCE) as reference electrode. The voltammograms of each radical displayed two quasireversible redox pairs, one corresponding to its reduction (O_1/R_1) and the other one to its oxidation (O_2/R_2), which are attributed to the equilibrium reactions involving the addition/removal of one electron to/from the trivalent central carbon atom to form its stable anion and cation, respectively (Scheme 5).

Values of the electrochemical parameters are compiled in Table 2 together with those for adduct **1**$^\bullet$,[14] and Figure 3 shows

SCHEME 5

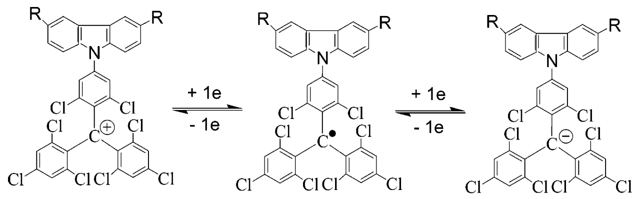


TABLE 2. Standard Potential for the Redox Pair Related to the Reduction (O_1/R_1) and Oxidation (O_2/R_2) of Radical Adducts $1^\bullet$−$7^\bullet$,[a] Difference between Their Anodic (E_a^p) and Cathodic (E_c^p) Peak Potentials, Electron Affinities, and Ionization Potentials

adduct	$E^o(O_1/R_1)^b$ (V) (($E_p^a - E_p^c)^c$ (mV))	$E^o(O_2/R_2)^b$ (V) (($E_p^a - E_p^c)^c$ (mV))	EA (eV)	IP (eV)
$\mathbf{1}^{\bullet d}$	−0.52 (130)	1.03 (130)	4.28	5.83
$\mathbf{2}^\bullet$	−0.54 (100)	0.86 (120)	4.26	5.66
$\mathbf{3}^\bullet$	−0.48 (110)	1.12 (100)	4.32	5.92
$\mathbf{4}^\bullet$	−0.42 (140)	1.27 (120)	4.38	6.07
$\mathbf{5}^\bullet$	−0.54 (120)	0.95 (110)	4.26	5.75
$\mathbf{6}^\bullet$	−0.47 (130)	1.18 (140)	4.33	5.98
$\mathbf{7}^\bullet$	−0.48 (140)	1.11 (120)	4.32	5.91

[a] CH_2Cl_2 solution (~10^{-3} M) with Bu_4NClO_4 (0.1 M) as background electrolyte on Pt electrode. [b] Potential values versus SCE (saturated calomel electrode). [c] Values at a scan rate of 100 mV s^{-1}. [d] Values taken from ref 14.

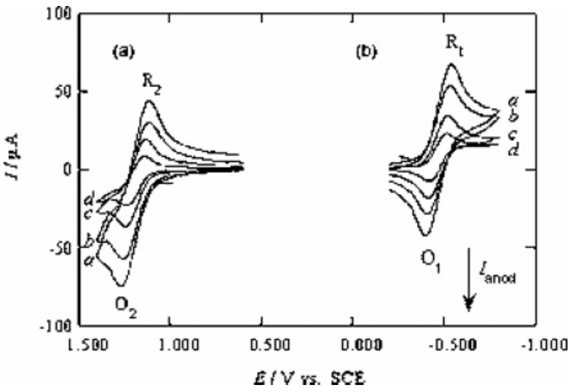


FIGURE 3. Cyclic voltammograms recorded for a 1 mM radical adduct $\mathbf{6}^\bullet$ solution in CH_2Cl_2 with TBAP 0.1 M on Pt at 25 C. (a) Oxidation at an initial and final potential of 0.600 V and a reversal potential of 1.400 V. (b) Reduction at an initial and final potential of −0.200 V and a reversal potential of −0.800 V. Scan rate: (a) 200, (b) 100, (c) 50, (d) 20 mV s^{-1}.

TABLE 3. UV−vis Absorption Data of the Spectra of Radical Adducts $1^\bullet$−$7^\bullet$ in $CHCl_3$ and Anion Adducts 1^-−7^- in THF

adduct	λ_{max}nm (ϵ)^a	λ_{max}nm (ϵ)^a (anion)
$\mathbf{1}^{\bullet b}$	374 (32 700), 560 (sh) (2700), 598 (3700)	508 (36 300)
$\mathbf{2}^\bullet$	373 (32 600), 647 (4400)	506 (33 100)
$\mathbf{3}^\bullet$	374 (30 700), 558 (sh) (2410), 585 (2840)	506 (38 400)
$\mathbf{4}^\bullet$	373 (30 700), 552 (1460)	507 (32 200)
$\mathbf{5}^\bullet$	375 (27 000), 581 (sh) (2160), 622 (3820)	506 (36 600)
$\mathbf{6}^\bullet$	373 (27 900), 543 (1840), 559 (1840)	509 (31 000)
$\mathbf{7}^\bullet$	374 (32 300), 556 (sh) (2190), 586 (2440)	510 (33 300)

[a] Units: $dm^3\ mol^{-1}\ cm^{-1}$. [b] Values taken from ref 14.

the cyclic voltammograms obtained for adduct $\mathbf{6}^\bullet$ (voltammograms for adducts $\mathbf{2}^\bullet$−$\mathbf{7}^\bullet$, see Figures S1−S12, Supporting Information). Each redox process, either in the cathodic or anodic region, is quasireversible because the difference between their anodic and cathodic peak potentials is always higher than the theoretical value of 59.2 mV expected for a one-electron reversible process and increases gradually as rising scan rate. Its standard potential ($E°$) was determined as the average of the anodic (E_p^a) and cathodic (E_p^c) peak potentials. The $E°$ value for the O_2/R_2 pair of the anodic region becomes more positive in the sequence $\mathbf{2}^\bullet < \mathbf{5}^\bullet < \mathbf{1}^\bullet < \mathbf{7}^\bullet \sim \mathbf{3}^\bullet < \mathbf{6}^\bullet < \mathbf{4}^\bullet$, in accordance with the electron-donating ability of substituents at the carbazolyl ring, adduct $\mathbf{2}^\bullet$ being the more easily oxidized. For the same reason, the $E°$ value for the O_1/R_1 pair of the cathodic region is shifted to more negative potential following the order $\mathbf{4}^\bullet < \mathbf{6}^\bullet < \mathbf{7}^\bullet \sim \mathbf{3}^\bullet < \mathbf{1}^\bullet < \mathbf{5}^\bullet \sim \mathbf{2}^\bullet$, adduct $\mathbf{4}^\bullet$ being the more easily reduced. Table 2 also collects the electron affinity (EA) and ionization potential (IP) values for adducts $\mathbf{1}^\bullet$−$\mathbf{7}^\bullet$ estimated from their standard potentials of the O_1/R_1 and O_2/R_2 pairs, respectively, taking a value of −4.8 eV as the SCE energy level relative to the vacuum level.[22]

Optical Properties. The spectral data of the UV−vis absorption spectra of carbazolyl-TTM radical adducts $\mathbf{1}^\bullet$−$\mathbf{7}^\bullet$ in $CHCl_3$ solutions are shown in Table 3. Two absorption bands are associated with the radical character of these radicals. The high-energy band corresponds to a $\pi \rightarrow \pi^*$ transition by virtue of their large molar extinction coefficients. This band at $\lambda \sim 375$ nm is not sensitive to the carbazolyl substituent. The second and very weak band with a slight multiplet structure is sensitive to the carbazolyl substituent. The absorption shifts from blue to red following the order $\mathbf{4}^\bullet < \mathbf{6}^\bullet < \mathbf{7}^\bullet \sim \mathbf{3}^\bullet < \mathbf{1}^\bullet < \mathbf{5}^\bullet < \mathbf{2}^\bullet$ depending on the electronic nature of the substituent. The alkoxy-substituted adduct $\mathbf{2}^\bullet$ is red-shifted 49 nm compared to $\mathbf{1}^\bullet$, which reveals a great interaction of the electron-donating methoxy moiety in the ground state, whereas the cyano-substituted radical $\mathbf{4}^\bullet$ is blue-shifted 46 nm with regard to $\mathbf{1}^\bullet$ due to the strong electron-withdrawing nature of the cyano group. The significantly large value of this absorption band in $\mathbf{2}^\bullet$ and the absence of vibronic structure suggest the formation of an intramolecular charge transfer from the electron-rich carbazolyl ring to the trivalent carbon atom.

The chemical reduction and oxidation of adducts $\mathbf{1}^\bullet$−$\mathbf{7}^\bullet$ were carried out by reaction in aqueous tetrahydrofuran solution to anion adducts $\mathbf{1}^-$−$\mathbf{7}^-$ by one-electron reduction with tetrabutylammonium hydroxide[23] and by the reaction in CH_2Cl_2 to cation adducts $\mathbf{1}^+$−$\mathbf{7}^+$ with antimony (V) pentachloride. Both series of charged adducts are stable in solution, and their UV−vis spectra have been registered. The absorption data of the spectra of anion adducts are shown in Table 3. All of them present a single and broad band with a maximum around 508 nm. The cation adducts show more complex spectra, and they deserve more research that is now in progress in our laboratories.

The luminescence emission spectra of radical adducts $\mathbf{1}^\bullet$ and $\mathbf{3}^\bullet$−$\mathbf{7}^\bullet$ are displayed in Figure 4. Tables 4 and 5 summarize the optical properties of radical adducts $\mathbf{1}^\bullet$−$\mathbf{7}^\bullet$ and their diamagnetic precursors **1**−**7**, respectively, determined from UV−vis and fluorescence measurements in a nonpolar solvent such as cyclohexane and in the one more polar $CHCl_3$. Note that the absorption maxima wavelength of the lowest energy transition for adducts $\mathbf{1}^\bullet$−$\mathbf{7}^\bullet$ are only reported in Table 4 because this is the only one sensitive to the polarity of the solvent. These transitions undergo small (1−5 nm) shifts in adducts $\mathbf{1}^\bullet$, $\mathbf{3}^\bullet$, and

---

(22) Alam, M. M.; Jenekhe, S. A. *J. Phys. Chem. B* **2002**, *106*, 11172−11177.

(23) The reducing properties of hydroxide anion on radicals of the perchlorotriphenylmethyl (PTM) series in nonaqueous solvents are well-known: Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267−445. Ballester, M.; Pascual, I. *J. Org. Chem.* **1991**, *56*, 841−844.

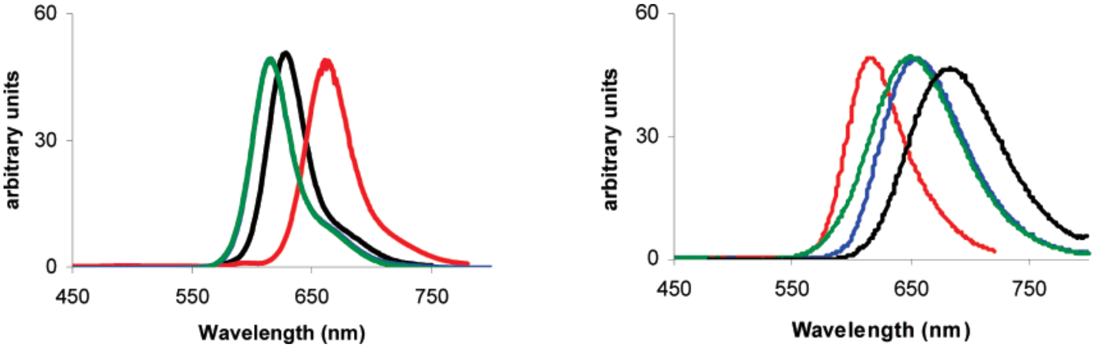


FIGURE 4. Normalized fluorescence emission spectra of radical adducts recorded in (left) cyclohexane solution; **1**$^{\bullet}$ black, **5**$^{\bullet}$ red, **3**$^{\bullet}$ blue, **7**$^{\bullet}$ green; (right): chloroform solution; **1**$^{\bullet}$ black, **6**$^{\bullet}$ red, **3**$^{\bullet}$ blue, **7**$^{\bullet}$ green; at room temperature.

TABLE 4. UV/vis and Luminescence Spectral Data for Radical Adducts 1$^{\bullet}$−7$^{\bullet}$

adduct	solvent	λ_{abs}^{a} (nm)	λ_{exc} (nm)	λ_{em} (nm)	Φ_F^{b}	Stokes shift (cm^{-1})
1$^{\bullet c}$	cyclohexane	603	515	628	0.53	660
	chloroform	598	515	680	0.02	2166
2$^{\bullet}$	cyclohexane	667	300		0	
	chloroform	647	300		0	
3$^{\bullet}$	cyclohexane	588	464	615	0.45	746
	chloroform	585	427	654	0.21	1803
4$^{\bullet}$	toluene	557	471	601	0.165	1314
	chloroform	552	471	591	0.12	1195
5$^{\bullet}$	cyclohexane	633	450	661	0.29	669
	chloroform	622	450		0	
6$^{\bullet}$	toluene	578	450	625	0.48	1301
	chloroform	559	450	618	0.38	1708
7$^{\bullet}$	cyclohexane	587	427	615	0.34	776
	chloroform	586	427	653	0.22	1751

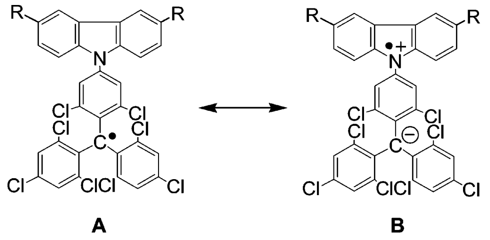
[a] The less energetic band in the absorption spectra. [b] Quantum yield of luminescence. [c] Values taken from ref 14.

TABLE 5. UV/vis and Luminescence Spectral Data for the Diamagnetic Precursors 1−7

precursor	solvent	λ_{abs}^{a} (nm)	λ_{exc} (nm)	λ_{em} (nm)	Φ_F^{b}
1^c	cyclohexane	335	300	338/353	0.05
3	cyclohexane	352	296	358/375	0.003
	chloroform	353	301	368/379	0.006
4	cyclohexane	insol			
	chloroform	340	304	346/361	0.20
5	cyclohexane	344	296	350/363	0.086
	chloroform	346	296	359	0.009
6	cyclohexane	insol			
	chloroform	296	301		0
7	cyclohexane	352	299	357/374	0.041
	chloroform	353	301	361/378	0.032

[a] The less energetic band in the absorption spectra. [b] Quantum yield of luminescence. [c] Values taken from ref 14.

7$^{\bullet}$ from cyclohexane to chloroform, whereas there is a blue shift in **5**$^{\bullet}$ (11 nm) and more significant shift in **2**$^{\bullet}$ (20 nm). Nothing is said with regard to adducts **4**$^{\bullet}$ and **6**$^{\bullet}$ due to their insolubility in cyclohexane. If values of both Tables 4 and 5 are compared, fluorescence emission is much more intense and dramatically red-shifted in radicals than in their precursors. In those radicals soluble in both solvents, the luminescence quantum yield is higher in cyclohexane than in chloroform. The luminescence of adducts **2**$^{\bullet}$ and **5**$^{\bullet}$ with electron-donor substituents in the carbazolyl ring deserves special mention. The complete absence of emission of **2**$^{\bullet}$ in both solvents and of **5**$^{\bullet}$ in chloroform suggests, at least in part, the existence of a donor−acceptor nature of the excited state with the consequent intramolecular charge transfer from the carbazolyl ring to the trivalent carbon atom in both radicals. It is known that the fluorescence efficiency in the intramolecular charge transfer states decrease with increasing strength of the transfer, and this is more significant in polar solvents.[24] A similar observation is also confirmed with the dramatic decrease of the fluorescence efficiency and the significant red-shifted emission in the luminescence of adduct **1**$^{\bullet}$ and in less extension to the luminescence of the adducts **3**$^{\bullet}$ and **7**$^{\bullet}$ with solvent polarity. The values of the Stokes shift (gap between the maxima of the first absorption and emission bands) of the emission of adducts **1**$^{\bullet}$, **3**$^{\bullet}$, and **7**$^{\bullet}$ were found to dramatically increase with the polarity of the solvent, thus supporting the charge-transfer character of their excited states. All of these observations suggest that adducts **1**$^{\bullet}$, **2**$^{\bullet}$, **3**$^{\bullet}$, **5**$^{\bullet}$, and **7**$^{\bullet}$ undergo structural reorientation in the excited state to adopt most probably a more planar conformation to facilitate a charge transfer from the carbazolyl moiety to the trivalent carbon atom. In accordance with it, the structure of the excited state should be in resonance with the canonical structures A and B:



The luminescence emission of adducts **4**$^{\bullet}$ and **6**$^{\bullet}$ should be different because of the electron-withdrawing character of the substituents in the carbazolyl ring. Since these radicals are not soluble in cyclohexane, toluene was chosen as a good solvent of low polarity. Both adducts **4**$^{\bullet}$ and **6**$^{\bullet}$ show fluorescence efficiency in toluene and chloroform, being a little lower in chloroform, and a blue-shifted emission with the polarity of the solvent, an opposite behavior to that shown by the other radicals.

Conclusions

We have established a new synthetic method to obtain a series of new carbazolyl derivatives with a pendant stable radical of the TTM series, radical adducts **2**$^{\bullet}$−**7**$^{\bullet}$. This method deals with the coupling between the carbazole nitrogen and a *p*-carbon center of the parent TTM radical. The results presented suggest

---

[24] Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315−7324.

that a radical mechanism is operative in this kind of reaction. Some of the adducts, **2**$^\bullet$−**5**$^\bullet$, are prepared by coupling between the TTM radical and the disubstituted N*H*-carbazoles, although some of them and other new ones **3**$^\bullet$, **6**$^\bullet$, and **7**$^\bullet$ are prepared by introducing the substituents into the carbazole ring once the radical adduct is made, without impairment of the radical character of the molecule. The EPR spectra, electrochemical properties, absorption spectra, and luminescence properties of these adducts have been studied. The redox behavior of these adducts exhibits electrochemical amphotericity being reduced and oxidized to their corresponding stable charged species in quasireversible processes. UV−vis spectra show the bands associated with the radical character of these adducts typical of the absorptions found in the stable radicals of the TTM series, involving two one-electron transitions from SOMO to LUMO and HOMO to LUMO, which correspond to the two first excited configurations. One of these transitions is sensitive to the carbazolyl substituents. All of the radical adducts except **2**$^\bullet$ show very significant luminescence properties, covering the red spectral band of the emission. They show a dramatic large red shift in emission when compared to their diamagnetic hydrocarbon counterparts, and the results evidence that the nature of the substituent controls the fine-tuning of the emission color. Furthermore, the radiative emission in those adducts with electron-releasing substituents in the carbazole ring is red-shifted with the polarity of the solvent and blue-shifted in those adducts with electron-withdrawing substituents in the carbazole. These facts indicate the donor−acceptor nature of the excited states in the electron-rich carbazole adducts. The EPR parameters of these radical adducts show practically an inestimable variation with the substituents in the carbazole. This fact suggests that delocalization into the carbazole is very limited; in fact, the hyperfine coupling to the N atom is imperceptible. From the results depicted in this paper, we have established structural groundwork to aid in the further design of new materials applicable in areas, where carbazole itself has demonstrated its usefulness.

Experimental Section

3,6-Diacetylcarbazole. Acetyl chloride (2.8 mL; 39.6 mmol) was added to a stirred mixture of carbazole (3 g; 18 mmol), $AlCl_3$ (5.33 mg; 40 mmol), and CS_2 (45 mL) at reflux in an anhydrous atmosphere. The mixture was further refluxed (6 h), and then the solvent was evaporated off and the crude was chromatographed in silica gel with chloroform to give 3,6-diacetylcarbazole (3.38 g, 75%): IR (KBr) 3277 (s), 1673 (s), 1662 (s), 1623 (s), 1599 (s), 1490 (w), 1451 (w), 1406 (w), 1358 (m), 1293 (m), 1267 (m), 1240 (m), 1227 (m), 1140 (w), 1127 (w), 1053 (w), 1021 (w), 956 (w), 904 (w), 882 (w), 829 (w), 820 (w), 802 (w), 638 (w) cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.79 (d, $J = 1.5$ Hz, 2H), 8.15 (dd, $J = 8.4$ Hz, $J = 1.5$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 2.77 (s, 6H, CH_3); UV (cyclohexane) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 260 (34 800), 292 (20 600), 325 (10 300) nm; EI-HRMS calcd for $C_{16}H_{13}NO_2$ 252.097984, found *m*/*z* 252.097546.

3,6-Diethylcarbazole. A mixture of $HgCl_2$ (2.5 mg), metallic Zn (26 g), and concentrated aqueous HCl acid (2.5 mL of HCl in 50 mL of water) was stirred at rt (15 min) to generate an amalgam. Concentrated aqueous HCl acid (40 mL) and 3,6-diacetylcarbazole (1 g; 5.99 mmol) were added, and the mixture was stirred vigorously (2 h) and then allowed to stand (12 h). Toluene (15 mL) was added, and the mixture was stirred to reflux (48 h). The resultant phases were separated, the aqueous phase was extracted with diethyl ether, and the combined organic phases were washed with water, dried, and evaporated to dryness. The residue was filtrated through silica gel with hexane to give 3,6-diethylcarbazole (417 mg, 47%): IR (KBr) 3417 (m), 2968 (m), 2926 (w), 2868 (w), 2853 (w), 1866 (w), 1765 (w), 1610 (w), 1574 (w), 1494 (s), 1465 (s), 1371 (w), 1326 (m), 1303 (m), 1248 (s), 1147 (w), 1055 (w), 920 (w), 883 (s), 813 (s), 752 (w) cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) 7.89 (s, 2H), 7.85 (s, 1H, NH), 7.32 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 2.83 (q, $J = 7.8$ Hz, 4H), 1.35 (t, $J = 7.8$ Hz, 6H, CH_3) ppm; EI-HRMS calcd for $C_{16}H_{17}N$ 223.136100, found *m*/*z* 223.136365.

[2,6-Dichloro-4-(3,6-dimethoxy-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl Radical Adduct (2$^\bullet$). (a) [2,6-Dichloro-4-(3,6-dimethoxy-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)-methane (2). A mixture of 3,6-dimethoxy-9*H*-carbazole[25] (200 mg; 0.9 mmol), tris(2,4,6-trichlorophenyl)methyl radical (486 mg; 0.9 mmol), anhydrous Cs_2CO_3 (486 mg; 1.4 mmol), and DMF (5 mL) was stirred at reflux (2.5 h) in an inert atmosphere and in the dark. The resulting mixture was poured into an excess of diluted aqueous HCl acid, and the precipitate was filtered off. The solid was chromatographed in silica gel with hexane/chloroform (1:2) to give tris(2,4,6-trichlorophenyl)methane (212 mg; 44%), identified by IR, and **2** (186 mg; 28%): IR (KBr) 3074 (w), 2934 (w), 2829 (w), 1594 (m), 1577 (m), 1542 (m), 1490 (s), 1471 (s), 1433 (m), 1372 (m), 1327 (m), 1205 (s), 1175 (m), 1157 (m), 1035 (m), 858 (m), 836 (m), 805 (s), 754 (m) cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 3.95 (s, 6H), 6.83 (s, 1H), 7.07 (dd, 2H, $J = 8.8$ Hz, $J' = 2.5$ Hz), 7.27 (d, 1H, $J = 2.1$ Hz), 7.29 (d, 1H, $J = 2.1$ Hz), 7.37 (d, 2H, $J = 8.8$ Hz), 7.40 (d, 1H, $J = 2.4$ Hz), 7.42 (d, 1H, $J = 2.4$ Hz), 7.45 (d, 1H, $J = 2.4$ Hz), 7.52 (d, 2H, $J = 2.4$ Hz), 7.58 (d, 1H, $J = 2.1$ Hz); MS (EI) 745.1 (M$^+$).

(b) Radical Adduct 2$^\bullet$. A mixture of **2** (85 mg; 0,11 mmols) and powdered sodium hydroxide (230 mg) in ethyl ether−dimethylsulfoxide (15 mL; 2:1) was shaken (48 h) at rt. The mixture was filtered into a solution of iodine (300 mg) in ethyl ether (20 mL), and the solution was stirred in the dark (1 h), washed with an excess of aqueous solution of sodium bisulfite and H_2O, dried, and evaporated to dryness, giving a residue which was chromatographed in silica gel with hexane/chloroform (1:2) to give adduct **2**$^\bullet$ (71 mg; 85%): mp 260 °C dec (DSC); IR (KBr) 3068 (w), 2931 (w), 2827 (w), 1577 (s), 1554 (m), 1523 (m), 1490 (s), 1471 (s) 1431 (m), 1371 (m), 1327 (m), 1204 (s), 1157 (m), 1036 (m), 857 (m), 829 (m), 809 (s) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 309 (24 600), 375 (32 400), 450 (sh) (2800), 647 (440); CI-HRMS calcd for $C_{33}H_{18}Cl_8NO_2$ *m*/*z* 739.884576, found 739.885621.

[2,6-Dichloro-4-(3,6-dibromo-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl radical adduct (3$^\bullet$). (1) From Tris(2,4,6-trichlorophenyl)methyl Radical (TTM). (a) [2,6-Dichloro-4-(3,6-dibromo-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methane (3). A mixture of 3,6-dibromo-9*H*-carbazole[26] (400 mg; 1.2 mmol), TTM (500 mg; 0.9 mmol), anhydrous Cs_2CO_3 (500 mg; 1.5 mmol), and DMF (5 mL) was stirred at reflux (2 h) in an inert atmosphere and in the dark. The resulting mixture was poured into an excess of diluted aqueous HCl acid, and the precipitate was filtered off. The solid was chromatographed in silica gel with hexane and 30% $CHCl_3$ to give tris(2,4,6-trichlorophenyl)methane (100 mg; 20%) identified by IR and **3** (245 mg; 33%): mp 346 °C (DSC); IR (KBr) 3075 (w), 1594 (s), 1577 (s), 1542 (s), 1468 (s), 1433 (m), 1371 (m), 1279 (s), 1229 (m), 1142 (m), 1056 (m), 1020 (m), 897 (m), 860 (s), 826 (s), 802 (s), 634 (m), 608 (m) cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 6.85 (s, 1H), 7.27−7.30 (m, 4H), 7.40−7.41 (m, 2H), 7.43 (d, 1H, $J = 2.4$ Hz), 7.54 (d, 2H, $J = 1.8$ Hz), 7.56 (d, 1H, $J = 2.1$ Hz), 8.18 (d, 2H, $J = 1.8$ Hz); UV (chloroform) λ_{max} /nm (/L mol^{-1} cm^{-1}) 303 (27 800), 338 (4500), 353 (4630) nm; MS (IE) 843.6 (M$^+$).

---

[25] Hsieh, B. R.; Litt, M. H. *Macromolecules* **1986**, *19*, 516−520.

[26] Smith, K.; James, D. M.; Mistry, A. G.; Bye, M. R.; Faulkner, J. *Tetrahedron* **1992**, *48*, 7479−7488.

(b) Radical Adduct 3$^{\bullet}$. A mixture of **3** (100 mg; 0,12 mmols), powdered sodium hydroxide (300 mg), and diethyl ether−dimethyl sulfoxide (15 mL; 2:1) was shaken (48 h) at rt. The mixture was filtered into a solution of iodine (400 mg) in diethyl ether (20 mL), and the solution was stirred in the dark (1 h) and then washed with an excess of aqueous solution of sodium hydrogen sulfite and H_2O, dried, and evaporated to dryness, giving a residue which was chromatographed in silica gel with hexane/chloroform (1:1) to give adduct **3**$^{\bullet}$ (80 mg; 80%): mp 350 °C dec (DSC); IR (KBr) 3069 (w), 1577 (s), 1556 (m), 1524 (s), 1468 (s), 1441 (m), 1429 (m), 1370 (m), 1279 (s), 1227 (s), 1182 (m), 1137 (m), 1021 (m), 861 (s), 814 (s), 802 (s) cm^{-1}; UV (CHCl$_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 374 (30 900), 445 (sh) (3550), 558 (sh) (2400), 586 (2800); CI-HRMS calcd for $C_{31}H_{12}Br_2Cl_8N$ *m/z* 841.680518, found 841.679882.

(2) From (4-*N*-Carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl Radical Adduct (1$^{\bullet}$). To a mixture of adduct **1**$^{\bullet}$ (200 mg; 0,29 mmol), silica gel (1.17 g), and anhydrous CH_2Cl_2 (8 mL) was added dropwise a solution of *N*-bromosuccinimide (100 mg; 0.58 mmol) in CH_2Cl_2 (10 mL) and the mixture stirred vigorously (5 h) at rt in the dark. The mixture was filtered, and the solution was washed with water, dried, and evaporated to dryness. The residue was chromatographed in silica gel with hexane and 30% CHCl$_3$ to give adduct **3**$^{\bullet}$ (198 mg; 80%).

[2,6-Dichloro-4-(3,6-dicyano-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl Radical Adduct (4$^{\bullet}$). (a) [2,6-Dichloro-4-(3,6-dicyano-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)-methane (4). A mixture of 3,6-cyano-9*H*-carbazole[27] (300 mg; 1.38 mmol), TTM (600 mg; 1.08 mmol), anhydrous Cs_2CO_3 (600 mg; 1.84 mmol), and DMF (5 mL) was stirred at reflux (2 h) in an inert atmosphere and in the dark. The resulting mixture was poured into an excess of diluted aqueous HCl acid, and the precipitate was filtered off. The solid was chromatographed in silica gel with CH_2Cl_2 to give tris(2,4,6-trichlorophenyl)methane (250 mg; 41%) identified by IR and **4** (153 mg; 19%): IR (KBr) 3075(w), 2220 (s), 1730 (w), 1630 (w), 1597 (s), 1576 (m), 1542 (s), 1482 (s), 1458 (m), 1435 (w), 1372 (m), 1335 (w), 1291 (m), 1242 (s), 1189 (w), 1175 (w), 1142 (w), 1077 (w), 1027 (w), 998 (w), 902 (m), 863 (m), 856 (m), 817 (s), 808 (s), 678 (w) cm^{-1}; CI-HRMS calcd for $C_{33}H_{13}{}^{35}Cl_6{}^{37}Cl_2N_3$ *m/z* 734.855869, found 734.856913.

(b) Radical Adduct 4$^{\bullet}$. A mixture of **4** (100 mg; 0,14 mmols) and powdered sodium hydroxide (250 mg) in ethyl ether−dimethyl sulfoxide (15 mL; 2:1) was shaken (48 h) at rt. The mixture was filtered into a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (55 mg; 0.20 mmol) in ethyl ether (20 mL), and the solution was stirred in the dark (2 h). The mixture was diluted with chloroform and washed with H_2O, dried, and evaporated to dryness, giving a residue which was chromatographed in silica gel with chloroform to give adduct **4**$^{\bullet}$ (70 mg; 70%): mp 379 °C dec (DSC); IR (KBr) 3062 (w), 2220 (s), 1630 (m), 1597 (m), 1577 (s), 1553 (s), 1524 (s), 1481 (s), 1457 (m), 1370 (m), 1358 (m), 1333 (w), 1292 (m), 1241 (s), 1183 (m), 1137 (m), 1083 (w), 1028 (w), 997 (w), 925 (m), 894 (w), 857 (m), 817 (s) cm^{-1}; UV (CHCl$_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 373 (28 200), 425 (sh) (5370), 499 (1700), 552 (1450); CI-HRMS calcd for $C_{33}H_{12}{}^{35}Cl_6{}^{37}Cl_2N_3$ *m/z* 733.848044, found 734.893018 (M$^+$ + H).

[2,6-Dichloro-4-(3,6-diethyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)Methyl Radical Adduct (5$^{\bullet}$). (a) [2,6-Dichloro-4-(2,6-diethyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)-methane (5). A mixture of 3,6-diethylcarbazole (300 mg; 1.35 mmol), TTM (500 mg; 0.9 mmol), anhydrous Cs_2CO_3 (500 mg; 1.5 mmol), and DMF (8 mL) was stirred at reflux (2 h) in an inert atmosphere and in the dark. The resulting mixture was poured into an excess of diluted aqueous HCl acid, and the precipitate was filtered off. The solid was chormatographed in silica gel with hexane/chloroform (9:1) to give **5** (115 mg; 17%): mp 281 °C (DSC); IR (KBr) 3072 (w), 2961 (m), 2927 (m), 2856 (w), 1726 (w), 1594 (s), 1577 (s), 1481 (s), 1436 (w), 1372 (m), 1329 (w), 1302 (w), 1233 (m), 1191 (w), 1174 (w), 1140 (w), 1075 (w), 1057 (w), 922 (w), 900 (m), 857 (s), 835 (m), 806 (s) cm^{-1}; ^{1}H NMR (300 MHz; CDCl$_3$) δ 7.92 (s, 2H); 7.60 (d, J = 2.1 Hz, 1H); 7.46 (d, J = 2.1 Hz, 1H); 7.42 (d, J = 2.1 Hz, 1H); 7.40 (d, J = 2.1 Hz, 1H); 7.37 (d, J = 8.4 Hz, 2H, 1-H); 7.30−7.25 (m, 4H); 6.84 (s, 1H, CH); 2.84 (q, J = 7.5 Hz, 4H); 1.34 (t, J = 7.5 Hz, 6H, CH$_3$); UV (cyclohexane) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 235 (53 600), 297 (20 700), 328 (17 300), 344 (7900) nm; CI-HRMS calcd for $C_{35}H_{23}Cl_8N$ *m/z* 740.927966, found 740.973128.

(b) Radical Adduct 5$^{\bullet}$. A mixture of **5** (115 mg; 17%), a hexane solution of TBAH (1.5M) (0.2 mL; 0.32 mmol), and THF (7 mL) was stirred (5 h) in an inert atmosphere at rt, and then 2,3-dichloro-4,5-dicyane-*p*-benzoquinone (36 mg; 0.16 mmol) was added. The solution was stirred in the dark (2 h) and evaporated to dryness, giving a residue which was filtered through silica gel with hexane to give adduct **5**$^{\bullet}$ (60 mg; 52%): mp 300 °C dec (DSC); IR (KBr) 2961 (m), 2927 (w), 1575 (s), 1555 (s), 1523 (s), 1479 (s), 1467 (s), 1372 (m), 1350 (m), 1329 (m), 1303 (w), 1232 (m), 1184 (m), 1136 (m), 1082 (w), 1059 (w), 925 (w), 857 (m), 811 (s), 797 (s), 761 (w) cm^{-1}; UV (CHCl$_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 240 (62 500), 297 (20 100), 375 (27 000), 452 (sh) (2250), 622 (3800); CI-HRMS calcd for $C_{35}H_{22}Cl_8N$ *m/z* 739.919740, found 739.907785.

[2,6-Dichloro-4-(3,6-diacetyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl Radical Adduct (6$^{\bullet}$). Acetyl chloride (0.8 mL; 1.12 mmol) was added to a stirred mixture of 4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (200 mg; 0.29 mmol), AlCl$_3$ (100 mg; 0.75 mmol), and CS$_2$ (8 mL) at reflux in an anhydrous atmosphere. The mixture was further refluxed (2 h) and then poured into an excess of diluted aqueous HCl acid and treated with CHCl$_3$. The organic solution, dried and evaporated to dryness, gave a residue which was chromatographed in silica gel with chloroform to give radical **6**$^{\bullet}$ (206 mg; 89%): mp 359 dec (DSC); IR (KBr) 3061 (w), 1678 (s), 1624 (m), 1593 (s), 1575 (s), 1554 (s), 1523 (m), 1478 (m), 1359 (m), 1290 (m), 1257 (s), 1217 (m), 1182 (m), 1137 (m), 858 (m), 815 (s), 799 (m), 757 (m); UV (CHCl$_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 263 (51 700), 293 (18 800), 328 (20 400), 373 (28 700), 555 (1900); MS (EI) 768.2 (M$^+$); CI-HRMS calcd for $C_{35}H_{18}Cl_8NO_2$ 767.878666, found *m/z* 767.888208.

[2,6-Dichloro-4-(3,6-dichloro-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl Radical Adduct (7$^{\bullet}$). (1) From [4-(*N*-Carbazolyl)-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)-methane (1). (a) [2,6-Dichloro-4-(3,6-dichloro-*N*-carbazolyl)phenyl] bis(2,4,6-trichlorophenyl)methane (7). A mixture of **1** (160 mg, 0.23mmol) and CH_2Cl_2 (3 mL) in a three-necked flask equipped with a septum and thermometer was cooled (0 °C) with vigorous stirring while SO_2Cl_2 (0.5 mL; 6 mmol) was added dropwise at such rate that the temperature did not exceed 2 °C. Then the cooling bath was removed, and the reaction mixture was stirred (2.5 h) at rt. The mixture was washed with water, dried, and evaporated to dryness to give a residue which was purified by chromatography on silica gel eluting with hexane/chloroform (3:1) to give **7** (140 mg; 81%): mp 329 °C (DSC); IR (KBr) 3075 (w), 1594 (s), 1576 (s), 1543 (s), 1476 (s), 1435 (s), 1372 (s), 1315 (m), 1278 (s), 1229 (m), 1141 (m), 1076 (m), 1024 (m), 900 (s), 856 (s), 804 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.85 (s, 1H), 7.28 (d, J = 2.1 Hz, 1H), 7.30 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.40−7.44 (m, 5H); 7.54 (d, J = 2.1 Hz, 1H); 8.03 (d, J = 2.1 Hz, 2H); UV (chloroform) λ_{max} /nm (ϵ/L mol^{-1} cm^{-1}) 302 (25 500), 339 (4400), 353 (4600) nm; MS (IE) 753.5 (M$^+$).

(b) Radical Adduct 7$^{\bullet}$. A mixture of **7** (100 mg; 0.13 mmols), powdered sodium hydroxide (300 mg), and diethyl ether−dimethyl sulfoxide (15 mL; 2:1) was shaken (48 h) at rt. The mixture was filtered into a solution of iodine (250 mg) in diethyl ether (20 mL), and the solution was stirred in the dark (2 h) and then washed with excess of aqueous solution of sodium hydrogen sulfite and H_2O, dried, and evaporated to dryness, giving a residue which was

---

[27] Patrick, D. A.; Boykin, D. W.; Wilson, W. D.; Tanious, F. A.; Spychala, J.; Bender, B. C.; Hall, J. E.; Dykstra, C. C.; Ohemeng, K. A.; Tidwell, R. R. *Eur J. Med. Chem.* **1997**, *32*, 781−793.

purified by column chromatography on silica gel with hexane/chloroform (1:2) to give adduct **7•** (72 mg; 72%): mp 334 °C dec (DSC); IR (KBr) 3070 (w) 1578 (s), 1555 (s), 1524 (s), 1474 (s), 1444 (m), 1371 (m), 1316 (m), 1279 (s), 1229 (m), 1183 (m), 1138 (m), 1076 (m), 1065 (m), 1024 (m), 924 (m), 857 (s), 804 (s), 754 (m) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 374 (32 400), 447 (sh) (2950), 556 (sh) (2200), 586 (2450); CI-HRMS calcd for $C_{31}H_{12}Cl_{10}N$ *m/z* 751.779602, found 751.782961.

(2) From [4-(*N*-Carbazolyl)-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl Radical Adduct (1•). A mixture of adduct **1•** (43 mg, 0.063 mmol) and CH_2Cl_2 (4 mL) in a three-necked flask equipped with a septum and thermometer was cooled (0 °C) and vigorous stirring, while SO_2Cl_2 (0.1 mL; 1.23 mmol) was added dropwise at such rate, that the temperature did not exceed 2 °C. Then, the cooling bath was removed and the reaction mixture was stirred (5 h) at rt. The mixture, washed with water, dried, and evaporated to dryness, gave a residue which was purified by chromatography on silica gel eluting with hexane to give adduct **7•** (23 mg; 43%).

[2,6-Dichloro-4-(3,6-dibromo-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methane (3). To a mixture of **1** (0.175 g; 0.25 mmol), silica gel (1 g), and anhydrous CH_2Cl_2 (7 mL) was added dropwise a solution of *N*-bromosuccinimide (0.091 g; 0.51 mmol) in anhydrous CH_2Cl_2 (8 mL) and stirred vigorously (5 h) at rt in the dark. The mixture was filtered, and the solution was washed with water, dried, and evaporated to dryness. The residue was chromatographed in silica gel with hexane and $CHCl_3$ (30%) to give **3** (0.145 g, 70%).

[2,6-Dichloro-4-(3,6-dicyano-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methane (4). A solution of radical adduct **4•** (200 mg, 0.29 mmol) and L-ascorbic acid (102 mg, 0.58 mmol) in a mixture of THF/H_2O (12 mL, 10:1) was stirred at rt (48 h) and then poured into an excess of diluted aqueous HCl acid and extracted with $CHCl_3$. The organic solution, washed with H_2O, dried over Na_2SO_4 anhydrous, filtered and evaporated, gave a residue which was chromatographed on silica gel with a mixture of hexane/chloroform (2:1) to give **4** (162 mg; 81%).

[2,6-Dichloro-4-(3,6-diacetyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methane (6). A mixture containing **1** (400 mg; 0.59 mmol), $AlCl_3$ (157 mg; 1.18 mmol), and CS_2 (28 mL) was stirred at reflux in a P_2O_5 atmosphere. Acetyl chloride (0.1 mL; 1.48 mmol) was added and evolution of gas was observed. After 2 h of reaction, the solvent was evaporated and the crude was treated with an ice/water/HCl mixture and extracted with chloroform. The organic layer was dried and evaporated to dryness and the resulting residue was chromatographed in silica gel with chloroform to give **6** (360 mg; 80%): mp 352 °C (DSC); ^1H NMR (300 MHz; $CDCl_3$) δ 8.31 (d, $J = 1.8$ Hz, 2H), 8.16 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.8$ Hz, 2H), 7.59 (d, $J = 1,8$ Hz, 1H), 7.47−7.42 (m, 5H), 7.32 (d, $J = 1.8$ Hz, 1H), 7.31 (d, $J = 1.8$ Hz, 1H), 6.88 (s, 1H), 2.76 (s, 6H, CH_3) ppm; IR (KBr) 3072 (w), 1678 (s), 1625 (w), 1593 (s), 1575 (m), 1541 (m), 1480 (m), 1458 (w), 1434 (w), 1421 (w), 1371 (m), 1359 (m), 1335 (w), 1303 (w), 1288 (w), 1258 (s), 1216 (w) 1192 (w) 1174 (w), 1141 (w) 1077 (w), 1024 (w), 996 (w), 959 (w), 901 (m), 855 (m), 835(w), 816 (m), 806 (m), 677 (w), 655 (w), 619 (m) cm^{-1}; UV (chloroform) λ_{max} /nm (ϵ/L mol^{-1} cm^{-1}) 263 (53 200), 296 (35 000) nm; MS (IE) 769.6.

[2,6-Dichloro-4-(3,6-diethyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methane (5). (a) From [2,6-Dichloro-4-(2,6-diacetyl-*N*-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl Radical (6•). A mixture of $HgCl_2$ (250 mg) and metallic Zn (3 g), HCl (0.3 mL) and water (5 mL) was stirred at rt (15 min) to generate an amalgam. Concentrated aqueous HCl acid (4 mL) and adduct **6•** (100 mg; 0.13 mmol) were added, and the mixture was stirred vigorously (2 h) and then allowed to stand (12 h). Toluene (9 mL) was added, and the mixture was stirred to reflux (48 h). The resultant phases were separated, the aqueous phase was extracted with diethyl ether, and the combined organic phases were washed with water, dried, and evaporated to dryness. The residue was filtrated trough silica gel with hexane to give **5** (34 mg; 35%).

(b) From [2,6-Dichloro-4-(3,6-diacetyl-*N*-carbazolyl)phenyl]-bis(2,4,6-trichlorophenyl)methane (6). A mixture of $HgCl_2$ (0.250 g), metallic Zn (3 g), water (5 mL), and concentrated aqueous HCl acid (0.3 mL) was stirred at rt (15 min) to generate an amalgam. Concentrated aqueous HCl acid (4 mL) and then **6** (150 mg; 0.20 mmol) were added, and the mixture was stirred vigorously (2 h) and left deposited (12 h). Toluene (9 mL) was added, and the mixture was stirred to reflux (24 h). The resultant phases were separated, the aqueous phase was extracted with ether, and the combined organic phases were washed with water, dried, and evaporated to dryness. The residue was filtrated trough silica gel with hexane to give **5** (105 mg; 71%).

Acknowledgment. Financial support for this research was provided by the Ministerio de Educación y Ciencia (Spain) through Grant No. CTQ2006-15611-C02-02/BQU. S.C. gratefully acknowledges the Generalitat de Catalunya for a predoctoral grant, and M.L. thanks the Institut d'Investigacions Químiques i Ambientals de Barcelona (CSIC) and the European Social Fund for his I3P fellowship. We also thank the EPR service of the Institut d'Investigacions Químiques i Ambientals de Barcelona (CSIC) for recording the EPR spectra.

Supporting Information Available: Cyclic voltammograms (Figures S1−S12) and EPR spectra (Figures S13−S18) for new radical adducts **2•**−**7•**. DSC diagrams for radical adducts **2•**−**7•** (Figures S19−S24). Details of computational methods, Cartesian coordinates, computed total energy of optimized structure of radical adduct **1•**. ^1H NMR (Figures S25−S30) and infrared spectra (Figures S31−S42) for new diamagnetic compounds **2**−**7** and infrared spectra for **2•**−**7•**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0708846