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[4-(*N*-Carbazolyl)-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl radical an efficient red light-emitting paramagnetic molecule

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Abstract—We report the synthesis, luminescent properties, electrochemical behavior and electron paramagnetic resonance of a novel stable radical adduct of the tris(2,4,6-trichlorophenyl)methyl radical and carbazole.

Carbazole and its derivatives are very attractive compounds by their electroactivity and luminescent properties. High photoconductivities and hole transporting properties of many polymeric materials can be greatly improved by incorporating carbazole as a pendant group in the framework.[1] Carbazole-containing compounds form relatively stable radical cations (holes) and many carbazole derivatives have a sufficiently high triplet energy to host red, full-color triplet emitters.[2] In addition, carbazole moiety is a convenient building block for the design and synthesis of molecular glasses, which are widely studied as the components of light-emitting diodes, and photorefractive materials.[3] The carbazole ring is easily functionalized and covalently linked to other molecules.[4] 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 have been published to obtain *N*-aryl derivatives of carbazole, by the use of Cu/bronze[5] or palladium catalyst.[6] Thus, different *N*-aryl azoles have been prepared from electron-rich and electron-poor halobenzenes as precursors, mainly bromobenzenes. This is an easy and direct way to successfully couple carbazole into polymers such as poly(*p*-bromostyrene).[7] Finally, another important property of carbazole derivatives for technological applications is their high thermal and photochemical stabilities.

In our research on stable organic radicals of the TTM (tris(2,4,6-trichlorophenyl)methyl radical (**1**)) series, we have focused our attention to the introduction of different substituents in the aromatic system of the TTM to modulate their electronic and electrochemical properties.[8] In this letter, we report the successful incorporation of TTM radical into carbazole. This allows us to combine the magnetic and redox properties of the TTM radicals and the luminescence properties of the carbazoles in view of their potential applications as chemosensors.[9] It is well known that stable nitroxide radicals are excellent fluorescent quenchers.[10] But in no case of the reported examples in the literature, the radical center is part of the fluorophore group of the molecule such as in the stable radical we report in this letter. The only published example in the literature of a carbazole coupled stable radical is a dimer-derived DPPH-type diradical.[11] TTM radical in dimethylformamide at reflux, in an inert atmosphere and in a short time (1 h), with an excess of carbazol in the presence of cesium carbonate gave as a majority product (33%), a mixture of (4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methane

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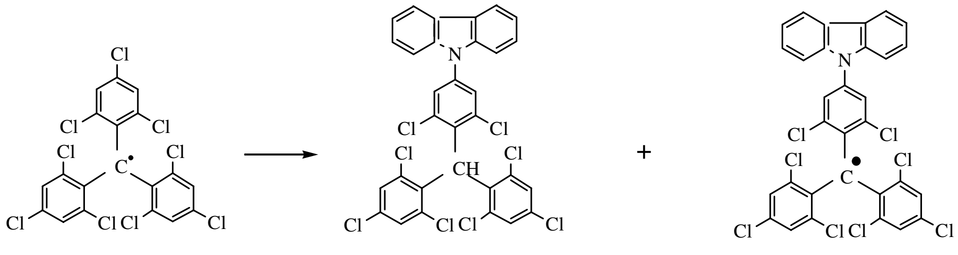
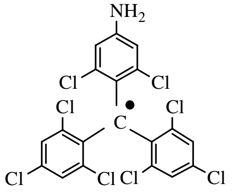
(**3**) with 4% of the corresponding radical **2**. The radical character of the molecule of TTM makes easy the substitution of the aromatic chlorine by the heterocycle. In this regard, it is worth mentioning that tris(2,4,6-trichlorophenyl)methane (α-H TTM) and 1,3,5-trichlorobenzene do not react at all with carbazole in the same conditions of temperature and time of reaction. Treatment of the mixture of **3** and **2** with an aqueous solution of tetrabutylammonium hydroxide followed by oxidation with chloranil rendered pure radical **2**.[12] Triphenylmethane **3**[12] was obtained in a quantitative yield by reduction of **2** with an excess of ascorbic acid in tetrahydrofuran–water overnight at room temperature. The stability of radical **2** has been tested in two organic solvents, chloroform and cyclohexane. After 24 h the decomposition is practically negligible.



1 **3** **2**



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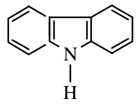

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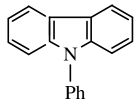

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The two absorption bands associated with the radical character of radicals **1**, **2**, and (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical[8c] (**4**) in chloroform solution are shown in Figure 1 and Table 1. The high values of the molar extinction coefficients of the first band indicate the $\pi^* \leftarrow \pi$ nature of this transition being the highest value in **1**. The absorption wavelengths are nearly the same in the three radicals ($\lambda \sim 375$ nm), suggesting that this transition is not sensitive to the presence of amino- and carbazole substitution. However, the second and weak band with a slight vibronic structure showed a remarkable red-shifted effect following the order **1** < **4** < **2** being in **2** and **4** of much higher intensity, indicating that radical **2** and **4** are significantly π-conjugated through the lone electron pairs at the nitrogen atom and that the unpaired electron is more delocalized. The UV spectrum of triphenylmethane **3** (precursors of radical **2**), in $CHCl_3$ solution shows bands at $\lambda(\varepsilon)$: 311(13,670) and 337(6550) nm.

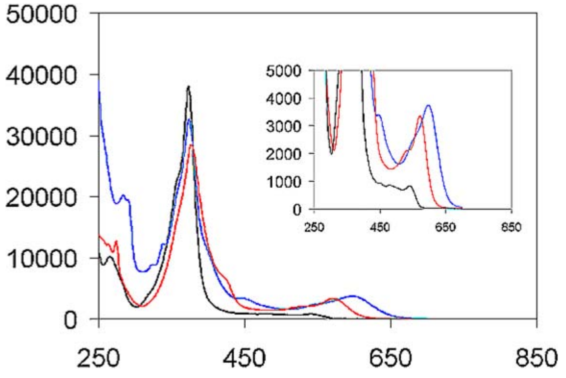

Figure 1. Absorption spectra of stable organic radicals **1** (black), **2** (blue), and **4** (red) in $CHCl_3$. The right-side of the graphic shows a detail of the less energetic band.

This new carbazole–TTM radical **2** exhibits intense fluorescence emission in cyclohexane in the red wavelength region (628 nm) (Table 2) compared to carbazole and radical **1** which show emission at 334/350 and 563 nm, respectively. The corresponding diamagnetic precursor, triphenylmethane **3** shows in cyclohexane emission peaks at 338 and 353 nm, in the same UV-region as carbazoles **5** and **6**, but with a low quantum yield of 0.05. So, we can strictly speak of a fluorescent stable organic radical. The emission wavelength and the efficiency of the fluorescence band of **2** in cyclohexane remains unaltered irrespective of the excitation wavelength (λ_{exc}, 515, 423, and 373 nm). This is possibly due to an efficient relaxation to the lowest excited state. The fluorescence maximum in **2** shows a considerable red shift and a large increase in the Stokes shift value on going from cyclohexane to a more polar solvent such as chloroform, providing evidence for a higher dipole moment of the molecule in the excited state than in the ground state. These effects suggest that **2** undergoes structural reorientation in the excited state to a more planar conformation with a significant intramolecular

Table 1. Wavelengths and absorptivities of the character radical bands in the electronic spectra[a] and redox and peak potentials[b] for the reduction (E_r^0) and oxidation (E_o^0) of radicals **1**, **2**, and **4**

Radical	λ nm (ε)[c]		E_r^0/V^d (V)	$E_p^a - E_p^c$ (mV)[e]	E_o^0/V^d (V)	$E_p^a - E_p^c$ (mV)[e]
1	373(38,150)	479(870) 542(840)	−0.51	100	1.27	100
2	374(32,670)	560(sh)(2710) 597(3740)	−0.52	130	1.03	140
4	377(28,500)	537(sh)(2080) 572(3430)	−0.83	110	0.31	100

[a] $CHCl_3$ solution ($\sim 10^{-4}$ M).

[b] CH_2Cl_2 solution ($\sim 10^{-3}$ M) with Bu_4NClO_4 ($\sim$0.1 M) on Pt.

[c] Units: $dm^3\ mol^{-1}\ cm^{-1}$.

[d] Potential versus SCE (saturated calomel electrode).

[e] Data at scan rate $100\ mV\ s^{-1}$.

Table 2. UV–vis and fluorescence data for radicals **1** and **2**, and carbazoles **3**, **5**, and **6**

		λ_{max} (nm)	λ_{exc} (nm)	λ_{em} (nm)	Φ_F^a	Stokes shift (cm^{-1})
1	Cyclohexane	537	395	563	0.03	860
	Chloroform	542	478	568	0.0015	844
2	Cyclohexane	603	515	628	0.53	660
	Cyclohexane/$CHCl_3$ 19:1	603	478	632	0.51	761
	Cyclohexane/$CHCl_3$ 9:1	603	478	633	0.47	784
	Cyclohexane/$CHCl_3$ 1:1	598	490	659	0.14	1548
	Chloroform	597	515	687	0.02	2257
3	Cyclohexane	335	300	338/353	0.05	1521
5	Cyclohexane	331	301	334/350	0.53	1640
	Chloroform	321/333	301	339/354	0.04	1781
6	Cyclohexane	339	301	343/359	0.43	1643
	Chloroform	328/341	301	349/363	0.08	1777

charge transfer from the carbazolyl moiety to the trivalent carbon atom. Furthermore, the quantum yield is highly dependent on the polarity of the solvent as shown for mixtures of cyclohexane and chloroform in Table 2. The yield is very low in chloroform, and an increase in the percentage of cyclohexane in the solvent mixture results in a large enhancement of the fluorescence efficiency. Preliminary tests of the fluorescence yields in CH_2Cl_2 show results still lower ($\Phi_F = 0.001$) and in more polar solvents such as acetonitrile and acetone radical **2** shows no fluorescence at all. This reduction or cancellation of the fluorescence suggests the existence of activated nonradiative decay processes that compete with the fluorescence decay.

Cyclic voltammogram of radical **2** was measured in CH_2Cl_2 solution ($\sim 10^{-3}$ M) containing tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte on platinum wire as working electrode using a saturated calomel electrode (SCE) as reference electrode. Radical **2** exhibits reversible oxidation and reduction processes attributed to the removal and addition of one electron from/to the trivalent carbon centered radical. Values of redox potentials are displayed in Table 1

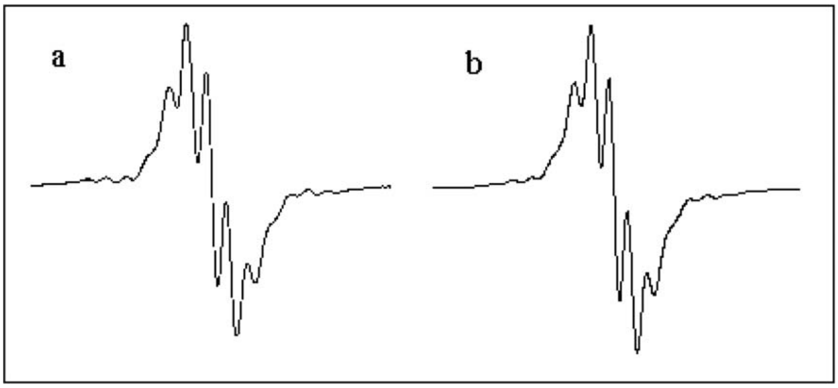

Figure 2. (a) EPR spectrum of radical **2** in CH_2Cl_2 solution at 193 K; (b) computer simulation.

along with those of radicals **1** and **4**. E^0 value for the reduction of **2** is similar to that of **1**, and E^0 value for the oxidation of **2** is much lower (240 mV) than that of **1**, in accordance with the donating ability of the carbazole placed at the *para* position of the phenyl group. The lowest E^0 value for oxidation corresponds to radical **4** (960 mV in relation to **1**).

X-band EPR spectrum of radical **2** was recorded in CH_2Cl_2 solution (Fig. 2). At 298 K the spectrum showed a single and broad band centered at $g = 2.0032 \pm 5$. The presence of the two small and broad lines in both sides of the main spectrum corresponded to the coupling of the free electron with the α ^{13}C nucleus with a coupling value $a = 28.0$ G. Approximately at 193 K, the spectrum consisted of an overlapped septet of lines due to the coupling with six aromatic protons ($a = 1.0$ G) and a small coupling with the nitrogen of the heterocyclic substituent ($a \sim 0.2$ G). The presence of two weak multiplets in both sides of the central band corresponded to the coupling with the three bridgehead ^{13}C nuclei of the molecule adjacent to the trivalent carbon atom ($a \sim 9.0$ G).

In summary, we have been able to incorporate a stable organic radical of the TTM series into a carbazole by a coupling reaction resulting in novel red-emitting-light radical adduct and we have shown the strong influence of the radical center in the emission properties of the carbazole. Work is now in progress in our laboratories to go through the mechanism of this reaction and to prepare other stable radicals of the TTM series by introducing electron-donor and electron-acceptors substituents into the carbazole system to modulate their emission properties.

Acknowledgements

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12. *Selected data for* **2** *and* **3**. Compound **2**: IR (KBr) 3068(w), 1573(s), 1553(s), 1522(s), 1492(m), 1477(w), 1461(s), 1368(m), 1322(m), 1306(m), 1281(w), 1232(m), 1183(m), 1137(m), 1076(w), 994(w), 922(w), 861(m) 814(m), 747(s), 722(m), 661(w) cm^{-1}; MS (MALDI-TOF): $m/z = 683.9$ (M^+). Anal. Calcd for $C_{31}H_{14}Cl_8N$: C, 54.4; H, 2.1; Cl, 41.5; N, 2.05. Found: C, 54.7; H, 2.0; Cl, 41.4; N, 2.0.

Magn. purity: $(4/g^2)\chi T = 0.396$ (theoretic value for $S = 1/2$: 0.375) (χ: magnetic susceptibility). Compound **3**: IR (KBr) 3063(w), 1598(s), 1578(s), 1541(s), 1491(m), 1465(s), 1451(m), 1440(w), 1420(w), 1368(w), 1317(m), 1232(s), 1076(w), 897(m), 861(s) 809(s), 748(s), 722(s), 680(w) cm^{-1}; MS (MALDI-TOF): $m/z = 684.9$ (M^+). Anal. Calcd for $C_{31}H_{15}Cl_8N$: C, 54.4; H, 2.2; Cl, 41.4; N, 2.0. Found: C, 54.5; H, 2.3; Cl, 41.7; N, 1.8.