

Stable radical cores: a key for bipolar charge transport in glass forming carbazole and indole derivatives†

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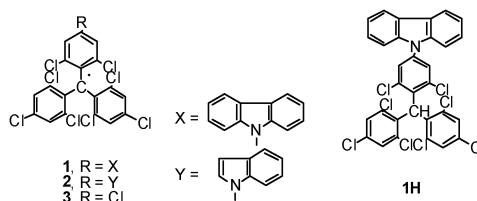
Stable radical adducts of the TTM series bearing carbazolyl or indolyl fragments show bipolar transport properties with mobility values among the highest detected in glassy small molecules. Bipolarity is attributed to the radical character, while the heterocyclic ring confers the adducts the glassy morphological states and the non-dispersive regimes for charge transport.

The interest in efficient charge carrier transporting molecular materials arises from the advantageous characteristics that they possess in comparison with traditional polymeric materials, such as easier purification methods, easier tunability, and easier characterization due to their small size and defined structure.¹

A challenging approach to obtain organic materials with high conductivities is the use of neutral or charged stable free radicals arranged in a crystal lattice, so that a half-filled energy band like in metals is generated by orbital overlapping between adjacent radicals. Aiming to achieve this target, Haddon *et al.* prepared a mixed valence salt which presented conductivities as high as 100 S cm⁻¹ at room temperature.² They also reported the preparation of neutral radicals among which some of the most highly conducting neutral organic solids can be found.^{3–5}

A different approach in the preparation of radical organic semiconductors with amorphous state was reported by Nishide *et al.*⁶ who developed a new kind of organic radical combining triphenylamine and nitroxide radical moieties. These radical adducts presented hole-transport by a hopping mechanism with mobility values in the order of 10⁻³ cm² V⁻¹ s⁻¹, which are comparable to the values found for typical hole-transporting organic materials.

As part of our target to develop the tris(2,4,6-trichlorophenyl)methyl (TTM) radical series to use them as electronic devices, we have recently reported two new radical adducts,



Scheme 1 Structure of radical adducts **1** and **2**, TTM radical **3**, and the diamagnetic precursor of **1**, **1H**.

(4(*N*-carbazolyl)-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**1**) and (2,6-dichlorophenyl-4-(*N*-indolyl))-bis(2,4,6-trichlorophenyl)methyl radical (**2**), by coupling carbazole and indole to TTM radical (**3**) (Scheme 1).^{7–10} These radical adducts show redox processes either of oxidation or reduction to stable charged species. This amphoteric electrochemical character, also observed in **3**,⁷ is attributed to the radical nature of these compounds.

Here we report the bipolar charge transport properties of **1** and **2**, thus presenting a new strategy to attain hole and electron mobilities in the same material, which is based on the electrochemical characteristics of its intrinsic radical nature. To the best of our knowledge, the only example in the literature on hole-transport in organic neutral radicals is the above mentioned Nishide's work, while no studies on the use of systems with an unpaired electron for either single electron-transport or both hole- and electron-transport have been reported.

Electrochemical parameters of radical adducts **1**⁷ and **2** (see ESI†) indicate that the main difference between them and their precursor, radical **3**,⁷ resides in their oxidation peak potentials and so, in their ionization potential (IP) values. IP values of radical adducts **1** (5.62 eV) and **2** (5.56 eV) are lower than that of **3** (5.86 eV), and they are comparable to those shown by hole-transporting materials based on triarylamine.¹ Therefore, the electron-donor nature of carbazole and indole moieties leads to the stabilization of the cations resulting from the oxidation processes of **1** and **2**. An EPR analysis of the isolated **1**⁺·SbCl₆⁻ salt† confirmed an intramolecular process of charge transfer from the carbazole moiety to the trivalent carbon. Therefore, the spectrum of a solution of **1**⁺·SbCl₆⁻ in CH₂Cl₂ at 2 K (Fig. 1) showed an intense single band ($g = 2.0030 \pm 0.0005$; peak to peak linewidth, $\Delta H = 8.3$ G) and a small half-field band ($g = 4.0090 \pm 0.0005$) that proved the existence of a triplet state at low temperatures. (Fig. 1).

Consequently, the cationic species presents a conformation that bears two unpaired electrons, one centered in the trivalent

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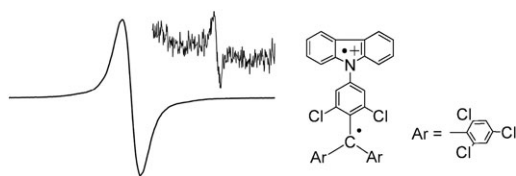


Fig. 1 EPR spectrum of a solution of 1^+SbCl_6^- in CH_2Cl_2 at 2 K. Insert shows the half-field band.

carbon and the other one in the nitrogen of the carbazole moiety.

Electron affinity (EA) values of **1** (4.20 eV), **2** (4.16 eV) and **3** (4.22 eV) are much higher than those reported in the literature for electron transporting organic semiconductors (EA \approx 2–3 eV). Therefore, the low level of the LUMO of these radicals improves their environmental stability and favors the electron injection from electrodes in n-channel transistors.¹¹

Radical adducts **1** and **2** show a great ability to form amorphous layers by spin-coating from THF or CHCl_3 solutions and, also in the case of **2**, by a rapid cooling from the melted state. They also present a high stability either in the neutral or in their charged (cation or anion) states.

Therefore, it is encouraging to study their hole and electron transport properties. Table 1 presents the charge drift mobilities of thin amorphous layers of pure radical adducts **1** (glassy transition temperature, $T_g = 80^\circ\text{C}$) and **2** ($T_g = 95^\circ\text{C}$),¹⁰ and of bisphenol Z polycarbonate blends of **1** (**1:PCZ**) and **2** (**2:PCZ**), measured by the xerographic time of flight (XTOF) technique.¹² Representative XTOF transients of holes for **1** are displayed in Fig. 2 (also see ESI†).

It is noteworthy that the measured electron-transport mobility values of pure materials **1** and **2** are among the highest reported values for low molar mass amorphous materials,¹ and that their hole-transport mobility values are comparable to those observed for molecular glasses based on carbazole.¹³ These results put them among the most efficient ambipolar molecular glasses reported in the literature so far.¹⁴

It is worthy to say some words about the correlation between molecular structure of **1** and **2** and their charge mobility properties. Charge transport in these radical adducts differs from charge transport in the usual organic semiconductors with an even number of electrons. Oxidation and reduction processes in the TTM radical series are attributed to the capability of the semi-occupied molecular orbital (SOMO)—which presents a major contribution of the localized p orbital of the trivalent carbon atom⁷—of losing its single electron or gaining one electron. Thus, the hole- and electron-transport for these materials might proceed through a non-bonding

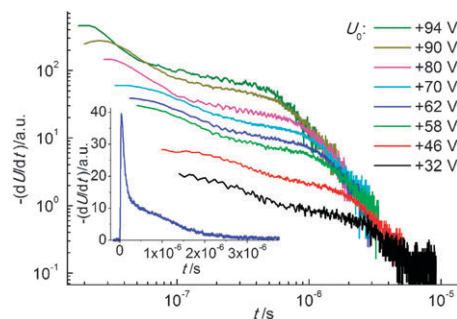


Fig. 2 XTOF transients of radical adduct **1**; insert shows one of the transient curves in linear plot.

SOMO orbital instead of through the traditional HOMO and LUMO orbitals, respectively.

XTOF measurements were also performed on the TTM radical (**3**) to study the role of the heterocycle moieties in the transport properties of **1** and **2**. Due to the rapid crystallization of the layers of pure material **3**, charge transport properties could only be evaluated in **3:PCZ** blend layers, which presented similar hole mobility values to those registered for **1:PCZ** or **2:PCZ** blends, although with a much more dispersive character. No electron-transport transient time could be detected in the log–log plot.

It is tempting to associate the deep trapping, responsible for the more dispersive hole-transport in the **3:PCZ** blend, to the greater localization of the hole in the p orbital of the trivalent carbon in **3** than in **1** and **2**. The charge transfer in the cationic species derived from **1** and **2** may imply a SOMO orbital with some participation of the heterocyclic moiety into the hopping process. However, the reasons for the different electron transport characteristics remain unclear and are the subject of further studies.

The relevance of the radical character in the semiconducting properties of the studied compounds was finally revealed by the study of the electrochemical and electronic behavior of the non-radical precursor of **1**, the compound **1H**⁷ (Scheme 1). Cyclic voltammetry studies of **1H** showed an irreversible oxidation and no reduction peaks. Accordingly, no charge drift mobility was observable in the XTOF experiments performed on this material. These results prove that the ambipolar charge transport of the radical adducts **1** and **2** can be unequivocally assigned to their open-shell electronic configuration.

In summary, the study of the charge-transport properties of stable radical adducts **1** and **2** by a time of flight potential discharge technique reveals that the combination of carbazole and indole fragments with a TTM radical core is an efficient

Table 1 Zero-field mobilities (μ_0), mobilities (μ) at an electric field of $6.4 \times 10^5 \text{ V cm}^{-1}$ in $\text{cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and field dependences (α) in $(\text{cm V}^{-1})^{1/2}$ of holes and electrons in amorphous layers of **1** and **2** and in the blends of **1**, **2** and **3** with polycarbonate (PCZ)

	Holes			Electrons		
	μ_0	μ	α	μ_0	μ	α
1	8.0×10^{-5}	4.6×10^{-4}	0.0023	7.5×10^{-4}	4.7×10^{-3}	0.0025
1:PCZ	3.0×10^{-7}	1.7×10^{-6}	0.0022	1.6×10^{-5}	6.5×10^{-5}	0.0017
2	1.4×10^{-4}	7.2×10^{-4}	0.0021	2.0×10^{-3}	7.8×10^{-3}	0.0017
2:PCZ	2.2×10^{-7}	1.6×10^{-6}	0.0025	2.2×10^{-4}	2.6×10^{-4}	0.0005
3:PCZ	3.3×10^{-7}	2.9×10^{-6}	0.0027	—	—	—

strategy to obtain molecular glasses showing ambipolar transport properties with high mobility values for both holes and electrons. While the bipolarity is attributed to the radical nature of the molecule, the heterocycle moiety provides the materials with the capability of glass formation and less dispersive regimes for charge migration. The electron mobility values found in these particular materials are among the highest so far reported for low molar mass amorphous materials.

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Notes and References

‡ This salt is a stable dark blue solid. Synthesis of $\mathbf{1}^+\cdot\text{SbCl}_6^-$: to a solution of **1** (380 mg; 0.6 mmol) in CCl_4 (20 mL) under N_2 atmosphere, SbCl_5 (0.27 mL; 2.1 mmol) was added. The reaction mixture was stirred at rt (2.5 h), and the resulting precipitate, filtered and washed with CCl_4 , resulted $\mathbf{1}^+\cdot\text{SbCl}_6^-$ (600 mg; quantitative yield); IR (KBr), 1612 (m), 1554 (s), 1523 (m), 1378 (m), 1296 (m), 1178 (w), 1134 (s), 859 (w), 815 (w), 714 (w), 522 (m) cm^{-1} . UV (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 936 (12570), 580 (sh, 4550), 516 (5000), 373 (10160). Anal. Calcd for $\text{C}_{31}\text{H}_{14}\text{Cl}_{14}\text{NSb}:\text{CCl}_4$ (1 : 1.6) C 31.04, H 1.12, N 1.11%. Found C 31.01, H 1.03, N 1.10%.

§ Charge drift mobilities were measured using the xerographic time of flight (XTOF) technique. Electric field inside the material layer was created by charging of a corona. Illumination with pulses of N_2 laser ($\lambda = 337 \text{ nm}$, 1 ns) generated charge carriers at the layer surface producing a decrease up to 1–5% of the initial potential before illumination. Surface potential decrease rate, dU/dt , was measured by the capacitance probe connected to the wide frequency band electrometer. Transient time (t_t) was thus determined from the kink in the log–log scale dU/dt curve or from the kink in the integral $\Delta U/t$ curves, in the case of electron transport in layers of pure compounds.

Drift mobility was then calculated according to the formula $\mu = d^2/U_{0\text{tt}}$, where d is the layer thickness and U_0 is the initial surface potential before laser pulse. Field dependences of the hole and electron mobilities were determined according to the formula $\log \mu = \alpha E^{1/2}$. The samples for the charge carrier mobility measurements were prepared by casting the tetrahydrofuran solutions of the pure radical adducts and of the molecular mixtures of radical adduct:polycarbonate in weight proportion 1 : 1 on polyester films and Al layer with a MC sublayer. The thickness of the charge-transporting layer varied in the range of 2 to 7 μm .

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