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Effects of vinylene and azomethine bridges on optical, theoretical electronic structure and electrical properties of new anthracene and carbazole based π -conjugated molecules.

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Abstract

This study aims to synthesize and characterize a new semi-conducting 2,7-distyrylcarbazole-based molecule (**M1**) and its Schiff-base analog (**M2**). Those two molecules were synthesized via Wittig-Horner and diamine condensation reactions, respectively. The effects of replacing the vinylene (-CH=CH-) linkage between carbazole donor unit and anthracene acceptor unit in molecule **M1** by an azomethine (-CH=N-) bridge in molecule **M2** on physicochemical and electrical properties are reported in this work. Thermal characterization shows a semi-crystalline morphology in solid state for the two organic materials and a good thermal stability up to 370C in the case of **M2**.

The observed non-fluorescence character of the Schiff-base molecule has been related to the photo-induced electron transfer (PET) process from the imine receptor moiety to the anthracene fluorophore unit. The effect of the addition of trifluoroacetic acid (TFA) on optical properties of the Schiff base molecule revealed a significant blue shift of the absorption spectrum and a turn-on of the fluorescence as well as visual changes. Computational analyses by Density Functional Theory (DFT) and time-dependent (TD-DFT) were then used to obtain conformation and the energy distributions of the molecular orbitals of the two compounds. The electrochemical behaviors were investigated by cyclic voltammetry and showed a reduction of the band gap of **M2** as compared to **M1** due to the electron-withdrawing effect of the azomethine (-CH=N-) bond. Finally, the charge-carrier mobility of the two compounds were extracted from single-layer diodes in the space-charge limited current regime (SCLC) and organic field effect transistors (OFETs) demonstrating lower hole mobilities in the case of **M2** based thin film devices. The hole effective mobility of **M2**

(measured by SCLC) was one order of magnitude higher after exposition to trifluoroacetic acid vapors than in neutral films.

Keywords: Anthracene; Carbazole; π -linkers; DFT calculations; Photo-induced electron transfer (PET); OFET.

Introduction

In the last decades, numerous organic semi-conducting materials have been designed, synthesized and characterized for optoelectronic applications. Those materials are based on the combination of aromatic or quinoïdal building blocks such as benzene, [1] thiophene, [2] pyrrole, [3] aniline, [4,5] fluorene, [6-9] anthracene [10], benzothiadiazole [11,12], thieno[3,2-*b*]thiophene [13] and thieno[3,4-*b*]thiophene [14] as well as carbazole [15] leading to an infinite variety of organic semi-conducting materials. As a consequence, organic optoelectronic devices have known a fast increase in performances. However, most of the organic conjugated materials suffer from a high degree of complexity that makes them expensive and difficult to elaborate in a large scale. Consequently, new approaches focusing on simple, cost-effective and easily scalable semi-conducting materials have emerged recently [16]. Owing to their well-defined chemical structure, small molecules are ideal candidates in this quest for simplicity and reproducibility [17].

In line with this idea, two simple and highly efficient blue emitting molecules (M_a [18] and M_b [19]) have been synthesized recently by attaching anthracene endcaps respectively at the 3,6 and 2,7-positions of a carbazole core (Figure 1).

Anthracene unit has been often used in organic semi-conducting materials as electron donor unit with a high thermal stability and good quantum efficiency in electroluminescence [20]. In combination with the carbazole unit, known as an excellent chemical building block for blue light emitting properties and organic solar cells [21, 22], suitable molecular structures have shown high efficiencies in optoelectronic devices. Despite the expected better physicochemical properties for M_b , [23] the optical properties of the two carbazole derivatives are very similar. This is probably due to the direct C-C bond used to connect anthracene residues to the carbazole core with a significant steric hindrance between neighboring conjugated units. Indeed, in addition to the aromatic unit composition, the optoelectronic properties of a specific molecular scaffold are also strongly depending on the nature of the chemical π -linker. The presence of π -bridges between aromatic systems plays an essential role in enhancing thermal, physicochemical, self-assembling and optoelectrical properties of conjugated organic molecules [24]. V. Tamilavan *et al.* [25] demonstrated that introducing rigid aromatic heterocycle spacers between conjugated units can improve the power conversion efficiencies (PCE) of solar cells. Arthur D. Hendsbee *et al* [26] have

shown that replacing thiophene by furan in a phthalimide-based conjugated molecule leads to a total loss of the electron mobility in organic field effect transistors (OFETs). In the present paper, we further explored the impact of chemical modifications of the π -linkers on the optoelectronic properties of the 2,7-carbazole based derivative discussed above. As new π -linkers, we considered the vinylene and the azomethine functions, as they should decrease the steric hindrance between aromatic units and consequently lead to a conjugation extension. Indeed, the introduction of vinylene bonds along the conjugated backbone, well studied in the literature [27-29], has shown to be an efficient approach to obtain lower steric hindrance, leading to higher backbone planarity and then to improved electrical properties [30-33]. Azomethine-based organic semi-conductors exhibit high thermal and environmental stabilities [34, 35], excellent mechanical properties [36] beside their ease of preparation [37] and in some cases, liquid crystalline behavior [38]. In addition, azomethine bridges, because of their pH-sensitivity, are widely used in sensors fields such as pH indicators [39] or fluorescence turn-on recognition of metals [40].

Thus, in this paper, we report on the synthesis of two new molecules, based on the functionalization with anthracene residues in the 2,7-positions of a carbazole unit via either a Wittig-Horner strategy or a diamine condensation reaction and on their full characterization of optoelectronic properties through among other OFET and diode elaborations.

1. Results and discussion

1.1. Synthesis and structural characterization

As discussed in the introduction, two new small molecules with chemical aromatic units linked either by vinylene or by azomethine π -bridges to give respectively the molecules **M1** and **M2** have been synthesized. Chemical structures of the studied models are presented in **Figure 2**.

As shown in **Scheme 1** and **Scheme 2**, the 2,7-bisfunctionalizedcarbazole derivatives (compound 10 and A4) have been prepared by a multi-step synthetic routes and were used on the synthesis of the two conjugated organic semi-conductors **M1** and **M2** respectively via Wittig-Horner reaction and condensation between carbonyl compound and primary aromatic amines reaction, respectively (**Scheme 2** and **Scheme 3**). The structures were confirmed with Fourier Transform InfraRed spectroscopy (**FT-IR**), proton and carbon nuclear magnetic resonance (^1H NMR and ^{13}C NMR) and high resolution mass spectrometry (HRMS).

The **N-2-ethylhexyl-2,7-bis(methylphosphonate)carbazole** (compound 10, **Scheme 1**) was carried out according to a reported procedure [41] and it was then allowed to react with an excess of

9-anthraldehyde (1.2 equivalent) in a mixture of potassium *t*-butoxide and tetrahydrofuran (THF) under inert atmosphere at 70°C. The target compound (**M1**) was obtained as a yellow cottony solid by purification of the crude mixture with flash column chromatography (Yield: 30 %).

The **FT-IR** spectrum of the 2,7-distyrylcarbazole showed the presence of the *E* vinylic (C=C) absorption peak at 966 cm⁻¹ [42]. The ¹H NMR revealed one doublet (2H, vinylic HC=CH, *J* = 16.4 Hz) at 8.21 ppm confirming the (*E, E*) configuration of the molecule. The **HRMS** of **M1** showed molecular ion peak at *m/z*=684.357.

The precursor 2,7-dinitrocarbazole (**A2**) was synthesized according to the procedure outlined in literature [43] and was then alkylated with 1-bromo-2-ethylhexane under basic conditions to give N-2-ethylhexyl-2,7-dinitrocarbazole (**A3**). Following synthesis route similar to that used in the preparation of N-alkyl-3,6-diaminocarbazole [44], **A3** was then reduced with SnCl₂ in a mixture of ethanol and ethylacetate (1:4) under nitrogen atmosphere at 70°C to give N-(2-ethylhexyl)-2,7-diaminocarbazole in a 90% yield. **M2** was finally synthesized by condensation reaction between N-(2-ethylhexyl)-2,7-diaminocarbazole (compound **A4**) and anthraldehyde in anhydrous methanol for 24h under inert atmosphere, the mixture was then cooled down to room temperature and the precipitated orange product was collected by filtration on a Büchner funnel (60% yield).

When comparing the **FT-IR** spectrum of **M2** with that of **M1**, we note the disappearance of the vinylene band at 966 cm⁻¹ and the appearance of two new bands at 1250 cm⁻¹ and 1590 cm⁻¹ attributed respectively to (H-C=N) in plane bending and (C=N) stretching vibrations of the azomethine bridge. The ¹H NMR spectrum reveals a singlet at 9.88 (2H) ppm corresponding to the azomethine (N=CH) proton. **HRMS** found for C₅₂H₄₃N₃: 686.3558 confirming the proposed structure of **M2**.

Theoretical studies of the vibrational frequencies for the two compounds **M1** and **M2** were performed by Density Functional Theory (DFT) calculations using B3LYP/6-311+G(d) method. Experimental and theoretical **FT-IR** spectra of the two molecules are shown in supplementary data (**Figure S.16** and **Figure S.21**). The most important vibrational waves with the proposed assignment are summarized in **Table 1**. Theoretically calculated vibrational modes are higher than the experimental values. This is at bottom due to the fact that the experimental measurements are conducted in solid state. However, theoretical studies are based on the hypothesis that the compound is in gaseous phase, in such condition, anharmonic effects are neglected. As shown in **Table 1**, the theoretical calculated wave numbers are in good agreement with the experimental FT-IR values.

Table 1. Selected experimental and calculated vibrational wavenumbers of **M1** and **M2** (cm⁻¹) and their assignment.

Compound M1		Compound M2		Assignments
Founded	Calculated	Founded	Calculated	
3080–3030 w	3236-3174 w-s	3080–3030 w	3267-3174 w-s	v (C–H) aromatic
	3155 w			v (C–H) vinylic
2964–2846 w	3000-3130 w-m	2960–2846 w	3131-3004 w-s	v (C–H) aliphatic
1456 m, 1620 w	1376 m, 1416 w, 1608 w, 1628 w, 1654 w, 1666 w, 1674 w, 1684 w	1453 m, 1620 w	1691-1572 w-s 1496-1456 w-m 1442-1321 w-m	v (C=C) aromatic
	-			v (C=N) symmetric
-	-	1590 w	1691w, 1687 w, 1680 w, 1649 s, 1642 s, 1630 m, 1602 m, 1571 w	
1620 w	1666 w, 1694 w, 1692 w, 1684 w, 1674 w	-	-	v(C=C) Vinylic
1320 w	1408 w, 1403 w, 1389 w, 1376 w	1320 w	1504 m, 1516 m	v (C–N)
-	-	1250 w	1315 w	δ (H–C=N)
966 m	994 w, 1011 w, 1014 w, 1016 w, 1019 w	-	-	γ (E–HC=CH) Vinylene
730 s	753 s	733 s	752 s, 776 w	γ (C–H) Aromatic

w: Weak, m: Medium, s: Strong. v :stretching, γ : out of plane bending, δ in plane bending.

The synthesized molecules are soluble in common organic solvents such as THF, DMF and halogenated solvents.

1.2. Thermal properties

Thermal properties of the synthesized compounds were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

TGA (**Figure 3 (a)**) shows that the two molecules exhibited good thermal stability up to 360°C for **M1** and 370°C for the imine compound under nitrogen flux, temperatures where 5 % of the models weights were lost. The replacement of vinylene linkage (-CH=CH-) between carbazole and anthracene units by the rigid azomethine (-CH=N-) group in molecule **M2** induced a significant increase in the thermal stability of the molecule.

The thermal transitions of the molecules have been studied by DSC and the curves are reported in **Figure 3 (b)** showing a similar thermal behavior. When the samples of the two materials were heated, an endotherm peak due to melting were observed for each model at 227°C and 182°C respectively for **M1** and **M2**. However, the higher melting enthalpy measured for **M2** highlights the higher crystallinity of this imine molecule compared to the more standard vinylic model.

1.3. UV-vis absorption

Photo-physical properties of **M1** and **M2** were investigated in chloroform solutions and in thin films by using ultraviolet-visible (UV-vis) and photoluminescence (PL) spectroscopies.

Figure 4 shows UV-Vis absorption spectra of the two materials studied in diluted chloroform solutions and in thin films.

The absorption spectra consists each one of two peaks. The absorption bands appearing in the range of 330–370 nm in chloroform solutions and in the solid films can be attributed to the $n-\pi^*$ transition bands of carbazole. The absorption peaks appearing toward 400 nm are assigned to the $\pi-\pi^*$ transition of the anthracene segment [45]. Whereas, the $n-\pi^*$ transitions of the azomethine linkage conjugated with aromatic nuclei exhibited characteristic absorption bands in the range of 370 to 455 nm [46, 47].

As seen in **Figure 4**, the synthesized Schiff-base (**M2**) has a red shifted and a slightly broadened UV-visible absorption spectrum as compared with that of **M1**. This is due to the azomethine ($-\text{CH}=\text{N}-$) bond between carbazole and anthracene in molecule **M2** which has an electron-withdrawing character [48]. Its presence contributes to the extension of the conjugation (i.e. increases the electron delocalization) leading to the reduction of the optical gap [49]. It's important to notice that both vinylene and azomethine spacers lead to more planar molecules as compared with aryl-aryl cross-coupled molecule. These π -bridges increase conjugation and induce a broadening of the absorption spectrum together with a reduction of the optical band gap from 3.05 eV for **M_b** to 2.69 eV and 2.49 eV for **M1** and **M2**, respectively.

DFT calculations have been performed using The Gaussian 09 program at the B3LYP/6-311 + G* level of theory in vacuum on the final molecules. The calculated frontier molecular orbital's (FMO) and the bandgap energies are reported in **Table 2**. The optimized geometries for **M1** and **M2** are depicted in **Figure 5**, and the frontier energy (HOMOs and LUMOs) distributions are presented in **Figure 6**. As shown in **Figure 5**, both molecules adopt (*E, E*) configurations and a very twisted conformation with high dihedral angles between the planar central-core (carbazole) and the adjacent ring of the anthracene moiety. This dihedral angle is higher in the case of **M1** (70°) than that of **M2** (60°). The calculated frontier energy distributions of **M1** are very extended over the molecular backbone. However, due to the electron effect of the azomethine ($-\text{CH}=\text{N}-$) linkage in the molecule **M2**, the LUMO is much localized on the anthracene moiety and the HOMO is much more extended over the molecular backbone (**Figure 6**). As it was expected, the introduction of the electron-withdrawing azomethine bridge withdraws electron density from the anthracene moiety.

This increases significantly the calculated electron affinity (EA) and slightly the ionization potentials (IP) resulting in a reduction of the HOMO-LUMO energy gap (**Table 2**).

The absorption spectra in thin films are highly broadened and red-shifted as compared with those in diluted solutions (20 nm for **M1** and 50 nm for **M2**), and the onset absorptions of the two materials in thin films are 481nm and 550 nm respectively for **M1** and **M2**. This red-shift was attributed to the π - π stacking, which results from the formation of aggregates in solid state [50]. We notice that a higher displacement of the absorption onset in thin films was observed in the case of **M2** indicating stronger π - π stacking interactions which can be attributed to the more important intermolecular interactions due to the better planarity of the Schiff base molecule as shown by DFT calculations (see below). The absorption data are summarized in **Table 2**.

Table 2. Optical spectroscopic parameters of **M1** and **M2** in diluted solutions and in thin films.

<i>Dilute solution</i>						
	$-X-$	$\lambda_{\max}$ (nm) ^(a)	$\epsilon_{\max}$ ($10^4 \cdot M^{-1} \cdot cm^{-1}$) ^(b)	FWHM (nm) ^(c)	λ_{onset} (nm) ^(d)	$E_{g\text{-opt}}$ (eV) ^(e)
M ₁	CH	349 ; 405	1.91 ; 3.1	105	460	2.69
M ₂	N	333 ^(f) ; 348 ; 369 ^(f) ; 389 ^(f) ; 421	1.11 ; 1.13 ; 1.26 ; 1.64 ; 1.1	140	500	2.49
<i>Thin films</i>						
		$\lambda_{\max}$ (nm) ^(a)	FWHM (nm)	λ_{onset} (nm)	E_{gap} (eV)	
M ₁	CH	344 ; 399	149	481	2.57	
M ₂	N	334 ; 445	219	550	2.25	

(a) Absorption peak maximum, (b) Molar extinction coefficient, (c) Full width at half maximum of the absorption spectrum in solution, (d) Absorption onset, (e) Optical band gap energy, (f) Shoulder

Table 3. HOMO, LUMO and Bandgap energies calculated by DFT.

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	Bandgap (eV)	$\vec{\mu}$ (debye)
M1	-4.86	-1.87	2.99	1.80
M2	-4.95	-2.21	2.75	1.67

1.4. Photoluminescence properties

The PL measurements were recorded at room temperature using freshly prepared diluted solutions ($2 \cdot 10^{-6}$ M). Fluorescence spectra are shown in **Figure 7**. In chloroform solution, **M1** PL spectrum shows one broad band in the blue-green region with a maximum at 500 nm which can be

attributed to the anthracene moieties [51,52]. Unfortunately, no photoluminescence was observed for **M2**. The chromaticity coordinates of the photoluminescence of **M1** in ($x = 0.45$ and $y = 0.46$) are presented according to the CIE 1931 color spaces in **Figure 7**.

The fluorescence quantum yields ϕ_{exp} were calculated from Eq (1).

$$\phi_{exp} = \phi_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{n^2}{n_{ref}^2} \quad Eq (1)$$

Where “I” is the integral of the corrected emission spectrum, “OD” denotes the optical density at the excitation wavelength and “ n ” is the refractive index of the medium. Quantum yield of **M1** was determined in solution by using cresyl violet as a reference $\lambda_{exc} = 400$ nm, $\phi = 0.5$ in ethanol and the value was 43% [53]. As shown previously, the fluorescence emission of the molecule **M2** was quenched. This quenching is probably partly due to the isomerization of the C=N double bond in the excited state [54] allowing a highly efficient photo-induced electron-transfer (PET) process [55,56].

In systems allowing the PET process, group containing non-bonding electron pair is usually separated by a short spacer from the fluorophore. The Schiff-base nitrogen atom and the electron-donating groups usually contain a relatively high-energy non-bonding electron pair. In this case, after excitation, an electron of the highest occupied molecular orbital (HOMO) is excited to the lowest unoccupied molecular orbital (LUMO), leaving a hole in the former orbital, that can be filled via a fast intramolecular electron transfer from the non-bonding electron pair of the nitrogen atom to the HOMO of the excited fluorophore. This phenomenon provides a mechanism for non-radiative deactivation of the excited state, resulting in the quenching of the fluorescence signal of the system [57]. The probable mechanisms of fluorescence emission of **M1** and PET process of **M2** are shown in **Figure 8**. This class of fluorophores is commonly used as sensors and act as indicators with changes in its fluorescence intensity upon complexation or dissociation [58]. These sensors can also function as pH indicators [59], protonation of the Schiff base annihilates the PET mechanism [60].

1.5. Effect of trifluoroacetic acid (TFA) on the optical properties of **M2**

In order to evaluate the PET mechanism, the optical properties of the **M2** molecule have been studied in acidic conditions. The effect of addition of TFA on the absorption spectrum in the diluted chloroform solution of **M2** is presented in **Figure 9 (Left)**. An important blue shift of the onset spectrum from 506 nm to 476 nm and a hypsochromic effect of the absorption band between 357 nm and 530 nm were observed. These shifts can be related to the formation of protonated species. After all, protonating azomethine linkage inhibits the $n-\pi^*$ transitions of the azomethine

linkage conjugated with aromatic nuclei and caused the disappearance of the associated absorption bond. The protonation of the nitrogen atom of the azomethine group prevents also the photoinduced electron-transfer (PET) phenomenon from nitrogen to anthracene fluorophore (**Figure 10**) inducing a naked eye remarkable color change from colorless to purple (**Figure 11 (a)**) and a “turn-on” of the fluorescence of the fluorophore with no significant shift of the emission maxima (**Figure 9 (Right)**). Both chloroform diluted solutions of **M2** in presence of TFA and **M1** have almost the same green emission under UV Lamp with 365 nm wavelength (**Figure 11 (b)**). This “Turn-On” system constitutes the basis for a proton (acid) sensing study including additional edges such as selectivity and sensitivity [61] and the compound is said to be fluorogenic.

1.6. Electrochemical Properties

The electrochemical behaviors of N-(2-ethylhexyl)-2,7-bis(vinyl-9-anthracene)carbazole (**M1**) and its Schiff base analog (**M2**) were investigated by cyclic voltammetry. The organic films were drop-coated onto a platinum working electrode from chloroform solutions and scanned both at positive and negative potentials at a scan rate of 100 mV s⁻¹. A Pt wire was used as counter electrode and Ag/Ag⁺ as reference electrode in a 0.1 mol.L⁻¹ solution of tetrabutylammonium tetrafluoroborate in dichloromethane.

The obtained cyclic voltammograms are shown in **Figure 12**. The lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO) and the electrochemical band gap values were calculated from the electrochemical onset potentials and by assuming that the energy level of the ferrocene/ferrocenium is 4.8 eV below the vacuum level as in the literature as follows [62].

$$E_{HOMO} (IP, \text{ionization potential}) = - (V_{onset-ox} - V_{FOC} + 4,8) \text{ eV} \quad Eq (2)$$

$$E_{LUMO} (EA, \text{electron affinity}) = - (V_{onset-red} - V_{FOC} + 4,8) \text{ eV} \quad Eq (3)$$

$$E_{g-el} = (E_{LUMO} - E_{HOMO}) \text{ eV} \quad Eq (4)$$

Where V_{FOC} is the ferrocene half-wave potential (0.405 V), $V_{onset-ox}$ is the model oxidation onset and $V_{onset-red}$ is the model reduction onset, all measured versus Ag/Ag⁺. The calculated electrochemical values are summarized in **Table 4**. The oxidation and reduction potentials of **M1** and **M2** are recorded in the range 0.90 to -2.20 V and 1.10 to -1.90 V, respectively. The obtained results showed that the ionization potential of **M2** was slightly increased as compared to that of **M1**, while, the LUMO level was significantly decreased. As a consequence, the measured electrochemical band-gap is reduced from 2.58 eV for **M1** to 2.36 eV in the case of **M2**, in good agreement with optical data. The **M2** electrochemical behavior is related to its Schiff base nature. Indeed, **M2** contains azomethine (–CH=N–) linkage in the structure which is known as an electron-

withdrawing [63] bond. In fact, the introduction of such electron-withdrawing group in conjugated systems induces an increase in electron affinity and in ionization potential [64-66].

To further understand the electronic structure of the synthesized molecules and to select electrodes materials for the charge injection (metal work function) in organic thin-film transistors [67-69] and OLEDs [70,71], it is essential to establish the relative positions of the characteristic electronic energy levels of these conjugated materials relative to vacuum and to compare them with those of MEH-PPV, ITO, Ca, Al and Au as presented in the energy diagram in **Figure 13**.

CV results showed that the two conjugated materials have around -5.10 eV HOMO energy and are *p*-type conjugated materials [72].

Table 4. Electrochemical onset potentials and electronic energy levels of **M1** and **M2**.

Compound	$E_{ox}(V)$	$E_{red}(V)$	$E_{HOMO}(eV)^a$	$E_{LUMO}(eV)^b$	$E_{g-el}(eV)^c$
<i>M1</i>	0.65	-1.93	-5.04	-2.46	2.58
<i>M2</i>	0.75	-1.61	-5.14	-2.78	2.36

^aHighest occupied molecular orbital ; ^bLowest unoccupied molecular orbital ; ^cElectrochemical band gap.

1.7. Electrical properties

1.7.1. Charge transport mechanism:

To investigate the current–voltage (I–V) characteristics of the two synthesized carbazole-based molecules, two single-layer devices with the [ITO/carbazole-based material/Al] structure were fabricated. The J–V (see **Figure S.23**) curves measured at room temperature indicate typical diode behavior with relatively low threshold bias voltages of 4.6 V and 4.9 V respectively for **M1** and **M2** (**Table 5**). The dynamic resistances (R_d) [73] are extracted and presented also in **Table 2**. As shown in the corresponding table, **M2** has the highest turn-on voltage and dynamic resistance demonstrating that **M2** is more resistant.

The J-V characteristics in a logarithmic scale of the two materials are presented in **Figure 14** and were used to determine the conduction mechanisms. The logarithmic plot shows three regions indicating three different regimes for each device:

- Region 1: at low voltage ($V < 2.6$ V) defining the Ohmic regime where the current density varies linearly with the applied voltage following equation [74]:

$$J_{\Omega} = q \cdot p_0 \cdot \mu \cdot V / d \quad Eq (5)$$

Where q is the electronic charge, μ is the charge mobility, p_0 is the free carrier density and d is the thickness of the film.

- Region 2: the medium voltage ($2.6 \text{ V} < V < 4.8 \text{ V}$ for **M1** and $2.6 \text{ V} < V < 5.2 \text{ V}$ for **M2**) where the current density is space-charge limited (SCLC regime) and the current density follows [75]:

$$J_{SCLC} = \frac{9}{8} \cdot \epsilon \cdot \mu_{eff} \cdot V^2 / d^3 \quad \text{Eq (6)}$$

where, ϵ is the permittivity of the organic material (assumed to $4\epsilon_0$ where ϵ_0 is the permittivity of vacuum). The μ_{eff} is the effective carrier mobility and is equal to $\theta\mu$, where θ is the fraction of free charge ($\theta = p/(p + p_t)$) and p and p_t are free and trapped charge-carriers densities, respectively).

- Region 3: at higher voltages, a trap filled SCLC regime with $J-V^m$ was measured ($m = 5$ and 6 respectively for **M1** and **M2**). When further increasing the voltage, free carriers that cannot be trapped again are introduced, resulting in a fast increase of the current intensity [76].

The hole effective mobilities (μ_{eff}) in the **M1** and **M2** films were calculated respectively as $6.2 \times 10^{-5} \text{ cm}^2/\text{V.s}$ and $8.4 \times 10^{-6} \text{ cm}^2/\text{V.s}$ (**Table 5**) by fitting the J-V characteristics to the SCLC model (**Eq. (6)**). The estimated charge-carrier mobilities are comparable to the achieved hole mobility in the MEH-PPV based device ($\approx 10^{-5} \text{ cm}^2/\text{V.s}$) [77].

Table 5. Dynamic resistances (Rd), threshold bias voltages (Vs) and the charge carriers values for the [ITO/molecule/Al] diodes.

	[ITO/M1/Al]	[ITO/M2/Al]
Dynamic resistance Rd (k Ω)	39	256
Threshold bias voltages Vs (V)	4.68	4.90
Charge carrier mobility (cm ² /V.s)	6.2×10^{-5}	8.4×10^{-6}

1.5. Effect of trifluoroacetic acid (TFA) on the electrical properties of [ITO/molecule/Al] device

Solution of compound **M2** (2.10^{-2} M) was prepared and spin-coated onto ITO/glass substrates. The device was exposed to TFA in vapor for 8 seconds (**M2** + TFA) before the deposition of the top Al electrode.

Figure 15 exhibits the effect of trifluoroacetic acid (TFA) on current density of the [ITO/**M2**/Al] single-charge-carrier devices.

The hole effective mobilities (μ_{eff}) in the **M2** and protonated **M2** in films were calculated using the usual formalism for SCLC devices (**Eq. (6)**) and are summarized in **Table 6**.

Table 6. The hole effective mobilities (μ_{eff}) in the neutral and protonated **M2** thin films.

<i>Compound</i>	<i>Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)</i>
M2	8.4×10^{-6}
M2 + TFA	8.0×10^{-5}

We note that the hole effective mobility in the **M2** thin film is substantially increased (almost one order of magnitude higher) after exposure to trifluoroacetic acid vapors for times as short as 8s. This sensitivity to protic acid makes this azomethine-based molecule a candidate to sensor applications.

1.7.2. Organic Field-Effect Transistors:

The output and transfer plots of the devices exhibited typical p-type OFET characteristics (**Figures 16 and 17**). The hole mobilities (μ) were calculated from the transfer characteristics of the devices in the saturation regime. The OFET characteristics (V_T and μ) are summarized in **Table 7**. The OFET hole mobilities are in the order of $(1.4 \pm 0.4) \times 10^{-6} \text{ cm}^2/\text{V.s}$ for **M1** and $(6.5 \pm 0.3) \times 10^{-7} \text{ cm}^2/\text{V.s}$ for **M2**.

Table 7. Bottom-gate/ Bottom -contact OFET characteristics of **M1** and **M2** thin films.

<i>Compound</i>	<i>Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)</i>	<i>V_T (V)</i>
M1	$(1.4 \pm 0.4) \times 10^{-6}$	-56
M2	$(6.5 \pm 1) \times 10^{-7}$	-28

Charge mobilities in **M1** films derived from OFET or deduced through J-V characteristics in the SCLC regime of single-layer diodes are higher than those of **M2** films. Surprisingly, the SCLC charge-carrier mobilities are 10 (**M2**) to 40 (**M1**) times higher than the OFET ones while the opposite was anticipated from the usual variation of mobility as a function of charge-carrier density [78]. The observed more than one order of magnitude higher out-of-plane hole mobility than the in-plane one suggests a high charge-transport anisotropy for these molecules as sometime observed in dumbbell shaped semi-conducting small molecules [69].

2. Conclusion

In summary, a 2,7-bisfunctionalized carbazole-based Schiff base (**M2**) and its distyrylcarbazole derivative (**M1**) were synthesized and characterized by different techniques. Both molecules have good solubility in common organic solvents. The structures of the compounds were confirmed by FT-IR, NMR, and HRMS. Thermal analysis showed a semi-crystalline behavior for

the two materials and higher thermal stability in the case of **M2**. Replacing the vinylene linkage of the molecule **M1** by the azomethine bridge which has an electronic withdrawing effect activates conjugation leading to a broader and red-shifted absorption spectrum and to the reduction of the optical gaps. The calculated frontier molecular orbital's (FMO) and the bandgap energies are found to be in good agreement with experimental data. In addition, the introduction of the C=N group induces a significant decrease in the HOMO energy level of the molecule.

The fluorescence quantum efficiencies of **M1** was 43% however the azomethine bond of **M2** turns off (quenches) the photoluminescence by photo-induced electron-transfer (PET) phenomenon.

The formation of the protonated species of the Schiff base by addition of TFA has a hypsochromic effect of the absorption spectrum and inhibits the PET process, inducing a turn-on of the fluorescence and a visible color change. Moreover, devices with [ITO/Semi-conductor/Al] configuration have shown relatively low turn-on voltages and three different mechanism conduction for each device. Low charge mobilities were extracted from SCLC regime of single-layer diodes and from field-effect transistors. An important increase of the hole effective mobility in the **M2** thin film (measured by SCLC) was noted after exposure to trifluoroacetic acid opening the field of sensor applications to such azomethine molecule.

Future work will focus on improving the electrical properties of the synthesized small molecules and investigating the electroluminescence of **M1**. Also the commendable sensitivity of molecule **M2** towards protic acid indicates the possibility of the development of the technique to further use in sensors research.

3. Experimental section

3.1. Reagents

4-bromobenzoic acid (98%), borane-dimethylsulfide complex (10 M in dimethylsulfide, magnesium sulfate, trityl chloride (97%), dimethylaminopyridine ($\geq 99\%$), triethylamine ($\geq 99.5\%$), 4-bromobenzyl alcohol (99%), n-butyllithium (2.5 M in hexanes), Trimethylborate ($\geq 98\%$), Palladium (II) acetate (98%), triphenylphosphine (99%), sodium hydride (60 % dispersion in mineral oil), tetrabutylammonium hydrogensulfate (97%), Thionyl chloride (Sigma–Aldrich, 97%), triethylphosphite (98%), sodium nitrile (99%), 4,4'-dinitro-2-biphenyl (98%), urea (98%), sodium azide ($\geq 99\%$), sodium sulfate ($\geq 99\%$), tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$), sodium bicarbonate ($\geq 99\%$), sodium *tert*-butoxide (97%), 9-anthraldehyde (97%) and 2-ethylhexylbromide ($> 97.0\%$) were supplied from Sigma–Aldrich and were used as received.

Fuming nitric acid, nitric acid, diethyl ether, dichloromethane, ethanol, concentrated HCl, hexanes, sulfuric acid, ethyl acetate, kerosene, petroleum ether, chloroform, N,N-

dimethylformamide (DMF), toluene, methanol, acetone and tetrahydrofuran (THF) were received from Sigma–Aldrich and were used without further purification and the last five solvents were dried by usual methods and distilled under reduced pressure.

The purity and the structure of the synthesized products were confirmed by Fourier Transform InfraRed spectroscopy (FT-IR), Nuclear Magnetic Resonance (NMR) and High Resolution Mass Spectrometry (HRMS). NMR and FT-IR spectra were recorded respectively on a Bruker Avance III 400MHz NMR spectrometer and a Perkin–Elmer Spectrum One FT-IR spectrometer (Thermo Scientific Nicolet IS50ATR) according to the Attenuated Total Reflectance (ATR) technique. HRMS experiments were performed on a Bruker micrOTOF-Q II spectrometer within the service center at the “Institut de Chimie” of Strasbourg University.

3.2. Synthesis and Characterization

^1H and ^{13}C NMR spectra of all compounds were recorded on Nuclear Magnetic resonance spectrometer Bruker Avance III HD with the magnet Bruker Ascent 400 MHz. **TF-IR** spectra were recorded on a Perkin–Elmer Spectrum UATR Two FT-IR spectrometer (Thermo Scientific Nicolet IS50ATR) according to the Attenuated Total Reflectance (ATR) technique. **HRMS** experiments were performed on a Bruker micrOTOF-Q II spectrometer within the service center at the “Institut de Chimie” of Strasbourg University. **DSC and TGA:** DSC measurements were performed using a METTLER Toledo DSC 1 instrument, operated at a scanning rate of 10°C/min. Thermogravimetric analyses (TGA) were conducted using a Hi-Res TGA Q5000 apparatus from TA Instruments under helium atmosphere (flow rate of 25 mL/min). Samples (2–4 mg) were heated from room temperature up to 400°C at a rate of 10°C/min. **UV-visible absorption and emission spectroscopy:** A Shimadzu UV-3600 dual-beam grating spectrophotometer with a 1 cm quartz cell was used on recording Uv–vis absorption spectra in chloroform diluted solutions ($5 \cdot 10^{-5}$ M) and in solid state. Thin films were drop coated from a dichloromethane (DCM) solution ($2 \cdot 10^{-2}$ M) onto glass substrate and the optical band gaps (E_g) were estimated from the onset absorption spectra using the Tauc relation $(\alpha h\nu) = A (h\nu - E_g)^{1/2}$, where $h\nu$ is the absorbed photon energy and α is the corresponding absorption coefficient [57]. The E_g was obtained from extrapolation to $\alpha = 0$ of the straight line portion in the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot. The steady-state fluorescence emission spectra were obtained by using a Horiba S2 Jobin Yvon Fluoromax 4 in chloroform diluted solutions ($2 \cdot 10^{-6}$ M) in order to avoid aggregation and reabsorption effects. Samples were excited with a 450 W Xenon lamp. **Cyclic voltammetry:** The electrochemical behaviors of the conjugated molecules were investigated by cyclic voltammetry with a BioLogic VSP potentiostat using platinum electrodes. A platinum wire and Ag/Ag⁺ electrodes were used respectively as counter electrode and reference

electrode in a 0.1 mol.L⁻¹ solution of tetrabutylammonium tetrafluoroborate [NBu₄][BF₄] in dichloromethane. The measurements were performed at room temperature, and the cell was degassed with argon before each scan. **Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT)** : Equilibrium geometry structures and the energy distributions of the molecular orbitals for the two the molecules have been performed in the gas phase using The Gaussian 09 software at the B3LYP/6-311 + G* level of theory in vacuum.

3.3. General synthetic procedure

3.3.1. Synthesis of N-(2-ethylhexyl)-2,7-bis(methylphosphonate)carbazole

The **N-2-ethylhexyl-2,7-bis(methylphosphonate)carbazole** (compound 10 Scheme 1) was synthesized according to a synthesis route described in the literature by N. Drolet *et al* [11].

3.3.2. Synthesis of N-(2-ethylhexyl)-2,7-bis(vinylene-(9-anthracene))carbazole (M1)

A mixture of compound (**11**) (0.58 g, 1 mmol), 9-anthraldehyde (0.50 g ,2.5 mmol), sodium *tert*-butoxide (0.38 g, 4 mmol) and dry THF (10 mL) were stirred under nitrogen atmosphere for 24h at room temperature. Then, the solvent was removed under reduced pressure, water was added (10 mL) and the organic layer was extracted with chloroform. After evaporating the solvent in vacuum, the residue was purified by flash column chromatography using a mixture of Ethyl acetate/Hexane (1:9, v/v) as eluent, to give the title product as a cottony yellow solid. M.P. 227°C (Yield: 30 %). ¹H NMR (400 MHz, CDCl₃, ppm): 8.49 (m, 6H, Ar); 8.21 (d, 2H, J = 16.4 Hz, H vinylic); 8.09 (m, 6H, Ar); 7.71 (dd, 2H, J = 8.0 and 0.8 Hz, Ar); 7.65 (s, 2H, Ar); 7.53 (m, 8H, Ar); 7.20 (d, 2H, J = 8.0 Hz, Ar); 4.31 (d, 2H, J = 7.6 Hz, N-CH₂); 2.2 (m, 1H, CH-(CH₂)₃); 1.40 (m, 8H, CH₂ aliphatic); 0.99 (t, 3H, J = 7.6 Hz, -CH₂-CH₃); 0.87 (t, 3H, J = 7.2 Hz, -(CH₂)₃-CH₃). ¹³C NMR (75 MHz, CDCl₃, ppm): 142.15 (Ar); 138.42 (Ar); 135.21 (Ar); 133.05 (Ar); 131.60 (Ar); 129.84 (Ar); 128.74 (Ar); 126.42 (Ar); 126.16 (Ar); 125.48 (Ar); 125.22 (Ar); 124.28 (Ar); 122.78 (Ar); 120.66 (Ar); 117.72 (Ar); 107.50 (Ar); 47.80 (N-CH₂); 39.48 (CH-(CH₂)₃); 30.95 (CH-CH₂-CH₂); 28.70 (CH₂-CH₂-CH₂); 24.43 (CH-CH₂-CH₃); 23.08 (CH₂-CH₂-CH₃); 14.06 (-CH₂-CH₃); 10.98 (-CH₂)₃-CH₃). **FT-IR** (cm⁻¹): 3080–3030 (w, aromatic and vinylic C–H stretching); 2964–2846 (w, aliphatic C–H stretching); 1456 m, 1620 w (m, aromatic C=C stretching); 1320 (w, C–N stretching); 966 (m, E-HC=CH out-of-plane bending); 730 (s, aromatic C–H out-of-plane bending). w: Weak, m: Medium, s: Strong

HRMS: Calculated for C₅₀H₄₃N: 683.92 Found: 684.36.

3.3.3. Synthesis of N-(2-ethylhexyl)-2,7-diaminocarbazole :

The **N-(2-ethylhexyl)-2,7-diaminocarbazole (Scheme 2)** were synthesized according to a modified procedure described in the literature by J.F. Morin *et al.* [58] as follow.

4,4'-dinitro-2-azidobiphenyl (A1): Sodium nitrite (7.98 g, 115.65 mmol) was gradually added to a solution of sulfuric acid (60 mL), 4,4'-dinitro-2-biphenyl (15 g, 57.9 mmol) in a mixture of acetic acid (300 mL) and at 0°C. The solution was stirred for 2h at 5-10°C, 7.50 g of urea followed by 750 mL of ice-water and 7.50 g of activated carbon were added. The solution was then stirred for 20 min and filtrated rapidly through a Buchner funnel into a 2 L flask immersed in ice. Sodium azide (5.07 g, 117 mmol) in 150 mL of water was added dropwise to the clear yellow filtrate. The resulting mixture was stirred for 1h at 0°C and for 24 h at room temperature. The solution was quenched with 700 mL of saturated aqueous solution of NaHCO₃ and extracted three times with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude material was recrystallized in ethanol to provide 12 g of the title product as a yellow solid M.P. 170°C (Yield: 72.5 %).

¹H NMR (400 MHz, Acetone-d₆, ppm): 8.38 (m, 2H); 8.25 (d, 1H, J = 2.4 Hz); 8.17 (dd, 1H, J = 8.4 and 2.4 Hz); 7.90 (m, 2H); 7.80 (d, 1H, J= 8.4 Hz). **¹³C NMR** (75 MHz, Acetone-d₆, ppm): 148.70; 147.90; 142.85; 139.35; 136.98; 132.23; 130.83; 123.32; 119.72; 114.47.

2,7-dinitrocarbazole (A2): Compound A1 (7.00 g, 24.5 mmol) was slowly added to 700 mL of boiling kerosene previously washed with concentrated sulfuric acid. The solution was stirred and refluxed for 1 h and kept at 0°C for 24 h. The obtained precipitate was filtered through a Buchner funnel. The crude product was washed with petroleum ether and recrystallized then in ethanol to give 5.54 g of the title product. M.P. > 300°C (Yield: 88%). **¹H NMR** (400 MHz, Acetone-d₆, ppm): 11.42 (s, 1H, N-H); 8.57 (s, 2H, Ar); 8.51 (d, 2H, J = 8.4 Hz, Ar); 8.17 (dd, 1H, J = 8.4 and 1.2 Hz, Ar). **¹³C NMR** (75 MHz, Acetone-d₆, ppm): 147.23; 141.06; 126.36; 122.11; 114.74; 107.64.

N-(2-ethylhexyl)-2,7-dinitrocarbazole (A3): A suspension of sodium hydride (NaH) (60% in oil, 1.60 g, 40 mmol) was gradually added to a solution of compound **A2** (5.144 g, 20 mmol) in dimethylformamide (DMF) (60 mL) at 0°C. The mixture was stirred for 1h, 1-Bromo-2-ethylhexane (30 mmol, 5.32 mL) was then added dropwise and the mixture was then allowed to react for 24h at room temperature. Ethanol was added to the resulting mixture to quench the remaining sodium hydride. The solution was poured into water, extracted four times with chloroform, washed several times with water and dried with anhydrous magnesium sulfate (Na₂SO₄). After evaporating the solvent in vacuum, the residue was purified by column

chromatography using a mixture of ethyl acetate/hexane (1:4, v/v) as eluent to provide 5.74 g of the title product as an orange crystalline solid. M.P. 81°C (Yield: 74 %). **¹H NMR** (400 MHz, Acetone-d₆, ppm): 8.52 (d, 2H, *J* = 2.0 Hz, Ar); 8.48 (d, 2H, *J* = 8.8 Hz, Ar); 8.14 (dd, 2H, *J* = 8.8 and 2.0 Hz, Ar); 4.48 (d, 2H, *J* = 7.6 Hz, N-CH₂); 2.2 (m, 1H, CH-(CH₂)₃); 1.45 (m, 8H, CH₂ aliphatic); 0.92 (t, 3H, *J* = 7.6 Hz, -CH₂-CH₃); 0.83 (t, 3H, *J* = 7.2 Hz, -(CH₂)₃-CH₃). **¹³C NMR** (75 MHz, Acetone-d₆, ppm): 148.12 (Ar); 142.74 (Ar); 126.78 (Ar); 123.08 (Ar); 115.52 (Ar); 106.92 (Ar); 48.31 (N-CH₂); 40.18 (CH-(CH₂)₃); 32.59 (CH-CH₂-CH₂); 31.30 (CH₂-CH₂-CH₂); 24.83 (CH-CH₂-CH₃); 23.58 (CH₂-CH₂-CH₃); 14.13 (-CH₂-CH₃); 11.12 (-(CH₂)₃-CH₃).

N-(2-ethylhexyl)-2,7-diaminocarbazole (A4) [44]: In a 250 mL flask, a mixture of compound A3 (1.67 g, 4.53 mmol), tin(II) chloride (SnCl₂) (10.22 g, 45.3 mmol), ethanol (27 mL) and ethyl acetate (36 mL) were stirred and refluxed for 24 h. The solution is allowed to cool down and then poured into ice. The pH was then made slightly basic (pH 7-8) by addition of saturated aqueous sodium bicarbonate solution before extracting with ethyl acetate. The organic phase was washed several times with brine, treated with charcoal and dried over magnesium sulphate. The evaporation of the solvent leaves 1.26 g of the title product as a pink solid. M.P. 74°C (Yield: 90 %).

¹H NMR (400 MHz, CDCl₃, ppm): 7.68 (d, 2H, *J* = 8.0 Hz, Ar); 6.56 (m, 4H, Ar); 3.90 (d, 2H, *J* = 7.6 Hz, N-CH₂); 3.75 (s, 4H, NH₂); 2.0 (m, 1H, CH-(CH₂)₃); 1.30 (m, 8H, CH₂ aliphatic); 0.90 (m, 6H, *J* = 7.6 Hz, -CH₃). **¹³C NMR** (75 MHz, CDCl₃, ppm): 143.85 (Ar); 142.50 (Ar); 119.76 (Ar); 118.72 (Ar); 108.11 (Ar); 94.98 (Ar); 47.39 (N-CH₂); 39.08 (CH-(CH₂)₃); 30.99 (CH-CH₂-CH₂); 28.88 (CH₂-CH₂-CH₂); 24.43 (CH-CH₂-CH₃); 23.13 (CH₂-CH₂-CH₃); 14.12 (-CH₂-CH₃); 11.00 (-(CH₂)₃-CH₃).

3.3.4. Synthesis of N-(2-ethylhexyl)-2,7-bis(azomethine-(9-anthracene))carbazole (M2)

In a 50 mL flask, a mixture of anhydrous methanol (15 mL), compound A4 (0.310 g, 1 mmol) and 9-anthraldehyde (0.44 g, 2.2 mmol) were refluxed under nitrogen for 24 h at 60°C. The solution was then cooled down to the room temperature and the orange precipitate was filtered through a Büchner funnel. The crude product was dissolved in chloroform, precipitated two times in anhydrous methanol and dried under vacuum to provide 0.411 g of the desired product as an orange solid product. M.P. 182°C (Yield: 60%). **¹H NMR** (400 MHz, CDCl₃, ppm): 9.88 (s, 2H, -N=CH); 8.85 (d, 4H, *J*=8.8 Hz, Ar); 8.60 (s, 2H, Ar); 8.22 (d, 2H, *J* = 8.0 Hz, Ar); 8.09 (d, 4H, 8.4 Hz, Ar); 7.59 (m, 8H, Ar); 7.53 (s, 2H, Ar); 7.41 (dd, 2H, *J*= 8.4 and 1.6 Hz, Ar); 4.28 (m, 2H, N-CH₂); 2.23 (m, 1H, CH-(CH₂)₃); 1.34 (m, 8H, CH₂ aliphatic); 0.95 (t, 3H, *J* = 7.6 Hz, -CH₂-CH₃); 0.83 (t, 3H, *J* = 7.2 Hz, -(CH₂)₃-CH₃). **¹³C NMR** (75 MHz, CDCl₃, ppm): 159.24 (-N=CH); 150.57 (Ar); 142.55

(Ar); 131.43 (Ar); 130.92 (Ar); 130.64 (Ar); 129.10 (Ar); 127.60 (Ar); 127.31 (Ar); 125.46 (Ar); 124.50 (Ar); 121.51 (Ar); 120.81 (Ar); 112.28 (Ar); 102.73 (Ar); 47.84 (N-CH₂); 39.24 (CH-(CH₂)₃); 30.90 (CH-CH₂-CH₂); 28.65 (CH₂-CH₂-CH₂); 24.30 (CH-CH₂-CH₃); 23.12 (CH₂-CH₂-CH₃); 14.04 (-CH₂-CH₃); 10.91 (-(CH₂)₃-CH₃). **FT-IR** (cm⁻¹) 3080–3030 (w, aromatic C–H stretching), 2960–2846 (w, aliphatic C–H stretching), 1453 m, 1620 w (m, C=C stretching), 1590 cm⁻¹ (w, C=N symmetric stretching), 1320 (w, C–N stretching), 1250 cm⁻¹ (w, H–C=N in plane bending), 733 (s, aromatic C–H out-of-plane bending). **HRMS**: Calculated for C₅₂H₄₃N₃: 685.35 Found: 686.3558.

3.4. Fabrication and characterization of the diodes

Solutions of the two small molecules (2. 10⁻² M in chloroform) were spin-casted (2500 rpm) onto indium tin oxide (ITO) glass to obtain a film with a thickness of 60 nm. After annealing at 40°C for 1 hour, a thin aluminum (Al) layer (150 nm) was deposited by thermal evaporation at 3×10⁻⁶ Torr. The current–voltage (I–V) characteristics of the devices were recorded with a Keithley 236 source meter using the ITO as an anode and the Al as a cathode.

3.5. Fabrication and characterization of OFETs

The charge transport was extracted from the electrical characteristics of organic field-effect transistors (OFET) configuration (bottom contact, bottom gate configuration).

The OFETs were elaborated on commercially pre-patterned test structures whose drain and source contacts are composed of 10 nm thick Indium Tin Oxide (ITO) bilayers and 30 nm thick gold. A 230 nm thick silicon oxide was used as gate dielectric and highly n-doped (3.10¹⁷ /cm³) silicon crystal as gate electrode. The channel length and width channel were 20 μm and 10 mm, respectively. The test structures were cleaned in swap, acetone and isopropyl alcohol for 15 min in and finally using ultra-violet ozone system respectively. Hexamethyldisilazane (HMDS) was then spin-coated (500 rpm for 5 s and then 4000 rpm for 50 s) and annealed at 130°C for 10 min. Solutions of the conjugated molecules in anhydrous 1,2-Dichlorobenzene (4 mg/mL) were finally spin-coated (1200 rpm for 60 s and 2000 rpm for 120 s). The substrates were then left under vacuum (<10⁻⁶ mbar) for 14 hours to remove residual solvent traces. The elaboration and characterizations of the OFETs were performed in nitrogen ambient [59]. The hole mobilities (μ) were calculated from the transfer characteristics of the devices in the saturation regime, at V_{DS}= -80 V using the related equation: I_{DS}= (W/2L)C_i(V_G-V_T)² where I_{DS} is the source-drain voltage, V_G is he gate voltage, V_T is the threshold voltage extracted from the measured I_D^{0.5}-V_g characteristic of the OFET devices by finding the intersection of the linear extrapolation of the curve at its maximum

slope point with the gate-voltage axis, W and L are the channel width and length and C_i is the capacitance per unit area of the SiO_2 layer [60].

Abbreviations

Al: Aluminum

Au: gold

Ca: Calcium

CIE 1931: Cambridge International Examinations

DFT: Density functional theory

DSC: Differential scanning calorimetry

FT-IR: Fourier-transform infrared spectroscopy

HOMO: Highest occupied molecular orbital

HMDS: Hexamethyldisilazane

HRMS: High resolution mass spectrometry

ITO: Indium Tin Oxide

LUMO: Lowest unoccupied molecular orbital

MEH-PPV: poly[2-méthoxy-5-(2-éthyl-hexyloxy)-1,4-phénylène-vinylène]

OFET: Organic field-effect transistor

OLED: Organic light emitting diodes

OPV: Organic photovoltaics

PET: Photo-induced electron transfer

PL: photoluminescence

TFA: Trifluoroacetic acid

TGA: Thermogravimetric analysis

^1H NMR: Proton nuclear magnetic resonance

^{13}C NMR: Carbon nuclear magnetic resonance

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FIGURE CAPTIONS

Scheme 1. Synthetic route to **M1**.

Scheme 2. Synthetic route to **M2**.

Figure 1. Chemical structures of **M1** and **M2**.

Figure 2. Chemical structures of 3,6-di(anthracen-9-yl)-9-ethyl-9H-carbazole (**M_a**) and 2,7-di(anthracen-9-yl)-9-ethyl-9H-carbazole (**M_b**).

Figure 3. ATG (a) and DSC (b) curves of **M1** and **M2**.

Figure 4. Normalized UV–Vis absorption spectra of **M1** and **M2** in chloroform diluted solutions and in thin films.

Figure 5. Face view (Left) and side view (Right) of the optimized molecular geometry for the minimal energy conformation for the **M1** and **M2**.

Figure 6. HOMOs and LUMOs frontier energy distributions for **M1** and **M2**.

Figure 7. (Left) Normalized PL spectra of **M1** and **M2**; in chloroform diluted solutions (2×10^{-6} M). **(Right)** the CIE chromaticity diagram of **M1**.

Figure 8. (a) Proposed fluorescence emission mechanism of **M1**. **(b)** The PET mechanism of **M2**.

Figure 9. Effects of **(a)** the addition 2 equivalents of acid (TFA) on the absorption profile and **(b)** of increasing concentration of acid (TFA) on the emission profile of **M2** in chloroform solvent. (Sample concentrations are 5×10^{-5} M for the absorption and 2×10^{-6} for the PL)

Figure 10. Switch-on fluorescence mechanism of **M2** in presence of TFA.

Figure 11. The photograph of **(a)** **M2** alone and in the presence of TFA (10 μ M) and **(b)** the photograph of **M2** alone, **M2** in the presence of TFA and **M1** under UV illumination.

Figure 12. Cyclic voltammograms of **M1** and **M2**.

Figure 13. Energy diagram of ITO, **M1**, **M2**, MEH-PPV, PC₇₁BM, Ca, Al and Au.

Figure 14. The J–V characteristic for the [ITO/molecule/Al] diode in log–log representation.

Figure 15. The J–V characteristics in linear (a) and logarithmic (b) scales of neutral and protonated **M2**.

Figure 16. Typical output curves **(a)** and transfer plots **(b)** of the bottom-gate/bottom-contact OFET devices for **M1**.

Figure 17. Typical output curves **(a)** and transfer plots **(b)** of the bottom-gate/bottom-contact OFET devices for **M2**.

RUNNING HEAD TITLE: New vinylene and azomethine linked anthracene based π -conjugated molecules.

M1 **M2**

New vinylene and azomethine linked carbazole based molecules were synthesized.

Azomethine group reduced the optical gap and quenched the fluorescence.

Addition of trifluoric acid turned-on the fluorescence of the Schiff base.

The OFETs based on M1 and M2 were elaborated

Molecule with vinylene linkers (M1) showed higher charge carrier mobilities.