Bipolar Luminescent Azaindole Derivative Exhibiting Aggregation-Induced Emission For Non-doped Organic Light-Emitting Diodes

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In this paper, a new D-A bipolar luminescent azaindole is synthesized and fully characterized. The triphenylamine (TPA) derivative acting as a hole-transporting unit (D) and 2-cyanoacrylic acid acting as electron-transporting unit (A) are incorporated in the same molecule. This luminogen, based on azaindole, presents aggregation-induced emission (AIE) characteristics. The theoretical calculations together with the photophysical characterization show the potential applicability of this new compound as electroluminescent material for non-doped OLEDs. A double-layer light-emitting device was developed showing that the presence of a better acceptor group in the azaindole derivative can reduce the electroplex and electromer formation in favor of the electron-hole recombination in the HOMO-LUMO of the molecule. These results pointed out the importance of molecular design of the emissive material for a better OLED performance.

1. Introduction

In recent decades, considerable efforts have been developed in the molecular design and characterization of organic luminescent conjugated molecules exhibiting a highly efficient fluorescence in solid state for fabricating high-performance organic light-emitting diodes (OLEDs).¹ Among all the strategies to reach that aim, the use of bipolar luminescent systems as electroluminescent materials has been pointed out as one of the most promising alternatives in this field. This is based on the fact that donor (D) and acceptor (A) groups are presented in the same conjugated molecule,² which favors the injection and the transport of the charges (holes and the electrons) and as a result improves the exciton recombination efficiency.³ Besides this, this donor-acceptor architectures offer the advantage of tuning the electronic and optoelectronics properties (ICT, intramolecular charge transfer) by modulating the energy levels of the molecules through the change of the donor or/ and the acceptor group presented in the molecule. It is worth to note that some works gave an account of D-A systems that could have aggregation-

induced emission (AIE) characteristics, where the luminogens improve their emission in aggregated state compared to liquid solution mainly by the restriction of the molecular motion.⁴⁻⁶ Therefore, the use of bipolar molecules with AIE characteristics combines two essential approaches to fabricate stable and efficient solid state emitters for OLEDs.⁷ However, sometimes these systems do not show the expected optoelectronic properties due to the presence of non-desired radiative electron-hole recombination channels involving e.g. excimers, exciplexes, electromers or electroplexes.^{8, 9} Consequently, an appropriate design of these bipolar systems is a key factor to the successfully of the building block emitters generation. In this paper, a D-A bipolar luminescent azaindole with AIE attributes in solid-state was synthesized (Scheme 1). The triphenylamine (TPA) derivative, which is supposed to act as a hole transporting unit (D), and the 2-cyanoacrylic acid, which is supposed to act as electron-transporting unit (A), are both incorporated in same molecule. Besides theoretical calculations the photophysical properties and applicability as electroluminescent material for OLEDs were investigated. The results confirm that this organic luminogen is a new kind of important and promising building block to construct solid-state emitters for OLEDs.

2. Experimental

2.1. Materials and methods

All starting materials were acquired from commercial suppliers. Column chromatography was carried out on silica gel (200-300 mesh). NMR spectra were obtained using a Bruker AVANCE 300 MHz and 75 MHz spectrometer. Chemical

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shifts (δ) are quoted in parts per million (ppm), referenced to the residual solvent. All the theoretical calculations were performed using the Spartan 14 software. The molecular geometries of the different compounds were optimized without symmetry constraints with density functional theory (DFT). The single energy point calculations were all computed at the B3LYP/6-311++G** level of theory and the vertical transition energies were calculated with time-dependent DFT (TD-DFT) at the B3LYP/6-311++G** level of theory. The UV-visible steady-state absorption and emission spectra were recorded using a Cary 100 Bio UV-visible or Lambda-950 spectrometer and a FLS920 Spectrofluorometer (Edinburgh Instrument Ltd, Livingston, UK), respectively. Stationary measurements have been recorded using Edinburgh FLS980 fluorometer where the Xe-lamp (the lamp uses to excite the sample) was blocked in order to only register the electroluminescence spectra. For the device fabrication an indium-tin-oxide (ITO)-coated glass substrates with a sheet resistance of $\sim 109 \Omega \text{ cm}^2$ was used as substrate. Before use, the substrates were first cleaned in an alkaline-detergent water (Hellmanex solution) using an ultrasonic bath during 10 min, followed by sonication for 10 min in consecutively water, acetone and isopropanol. Afterwards, the cleaned ITO-glasses (30 min) were subjected to an ultraviolet-ozone treatment to enhance the work function of ITO layer. On the cleaned ITO substrates, a solution of the hole injection layer, PEDOT:PSS (Sigma Aldrich, high conductivity), was spin coated at 3000 rpm for 120 seconds and subsequently annealed at 150 °C during 15 minutes. Afterwards, the emissive (EM) layer of compound **2**, was spin coated at 1000 rpm for 60 seconds using a solution of 20 mg/ml of **2** in CH_2Cl_2 . Next, the electron injection layer, 2-(4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD, Sigma Aldrich), was spin coated at 5000 rpm for 120 seconds (in cyclohexane) and annealed at 80 °C for 15 minutes. Finally, a 150 nm Aluminum (Al) electrode was thermally evaporation under high vacuum on top of the organic layer. Al was chosen for their low work function and higher stability to oxygen compared to other low work function metals like alkaline earth metals (Ca, Mg,) used earlier. All IV-curves were measured in the dark at room temperature using a Keithley 2400 device.

3. Results and discussion

3.1. Synthetic procedure

The synthesis of **2** from **1**¹⁰ proceeds via the Knoevenagel condensation: addition of an excess of 2-cyanoacetic acid with piperidine in dichloromethane and acetonitrile allowed to obtain compound **2** in a 49% yield (see Scheme 1). The synthesized derivative was identified by NMR, UV-vis spectroscopy and mass spectrometry (see Supporting Information).

Scheme 1. Synthesis of compound **2**

In the UV-visible absorption **2** exhibits a strong absorption band around 379 nm with a bathochromic shift compared to **1**. The behavior of compound **2** under heating was studied by thermogravimetric analysis (TGA). A 5% weight loss occurs at 269 °C demonstrating the high thermal stability of **2** (see Supporting Information).

3.2. Theoretical calculations

Density functional theory (DFT) calculations have been performed to investigate the geometries, frontier orbital energy levels and nature of the transitions to the excited state of compound **2**. The optimized molecular geometry of **2** shown in Figure 1A reveals that the dihedral angle between the azaindole moiety and the phenyl unit of the triphenylamine moiety is about 38°, while the dihedral angles between the phenyl units of the triphenylamine moiety are in the range 43–63°, typical of this building block.¹¹

Figure 1. (A) Optimized molecular geometry and (B) frontier molecular orbitals and energies for **2** calculated at the B3LYP/6-311G* level of theory.

The isodensity surfaces and energy of the frontier molecular orbitals of **2** are displayed in Figure 1B where the HOMO and LUMO orbitals are clearly distributed in separated regions of the molecular structure. The HOMO orbital (-5.3 eV) is mostly found at the triphenylamine group as expected due to the electron-rich nature of this substituent, whereas the LUMO orbital (-2.4 eV) is mainly localized at the cyano and carboxylic groups and partially at the azaindole moiety. TD-DFT calculations have derived a lowest-energy transition with an entire HOMO $\rightarrow$ LUMO character at an energy of 2.54 eV. Considering the features of the HOMO and LUMO orbitals (Figure 1B) this suggests that the lowest energy transitions is an intramolecular charge transfer (ICT) band.¹² Other calculated transitions are centered at 3.54, 3.70 and 3.82 eV, and are all mainly connected with transitions from the HOMO orbital to higher unoccupied orbitals.

3.3. Photophysical studies

Figure 2 shows the normalized absorption and emission spectra of **2** in toluene (purple lines). The absorption spectrum exhibits two narrow peaks centered at 310 and 375 nm. The high-energy peak is ascribed to a local electronic excitation, reminiscent of the absorption in the azaindole moiety,¹² while the low-energy peak could be attributed to a charge transfer transition taking into account the strong electron donor and acceptor character of the triphenylamine and cyano-carboxylic groups, respectively.¹³ This would also be in agreement with the results of the TD-DFT calculations. Moreover, there is virtually no mismatch in the absorption spectra of **2** measured in solvents with different polarity which suggests a low value of the dipole moment in the ground state (see Figure S2). The blue shift in THF is due to the smaller refractive index and polarizability of THF compared to the other solvents. Figure 2 also discloses the emission spectra of **2** in toluene upon excitation at $\lambda_{\text{exc}} = 400$, showing a broad peak centered at 535 nm, which is a mirror-image of the low-energy absorption peak. The study of the emission spectra of **2** in different solvents displays a double behavior depending on the solubility of **2** in each solvent. Thus, the emission spectra of **2** in solvents with moderate polarity (high solubility of **2**) reveal a reduction of the emission intensity and a bathochromic shift of the maximum of the emission upon increasing the polarity of the solvents, from toluene to CH_2Cl_2 (see Figure S3 and S4). This indicates a significant excited state dipole moment, agreeing with a transition with ICT character. One should note that in the polarizable solvents as toluene, anisole, CHCl_3 and CH_2Cl_2 the red shift of the emission maximum and the decrease in intensity are larger than what would be expected only on the basis of the dielectric constant or Δf . Such behavior has also been observed for other molecules with an excited state with CT or ICT character.^{14, 15} The decreased intensity in solvents with higher polarity is ascribed to the presence of a non-radiative deactivation process *via* a conical intersection involving a twisting of a single bond followed by a complete charge separation between the donor and acceptor units, an intramolecular charge transfer (ICT) process (see the Supporting Information for a more detailed discussion).¹⁶ On the other hand, the position of the emission band in solvents with extreme values of polarity (and a low solubility of **2**, cyclohexane and acetonitrile) is practically the same ($\lambda_{\text{em}} \approx 505$ nm), indicating a fluorescence from the same polarity-

independent excited species (Figure S3). The time-resolved emission measurements of **2** clearly support these double behavior (see Table S1). While mono-exponential fluorescence decays and a decrease of the fluorescence decay time upon increasing solvent polarity from 1.43 to 0.15 ns is observed for solvents with high solubility of **2**, a bi-exponential fluorescence decay is observed in cyclohexane and acetonitrile. In these solvents most of the emission is due to a component with a decay time of 10 and 7.5 ns for cyclohexane and acetonitrile, respectively. One should note that the solvent polarity dependence of the emission maximum and intensity is also observed for mixtures of cyclohexane and CH_2Cl_2 where upon increasing concentration of CH_2Cl_2 a red shift and decreased intensity is observed (Figure S4). We have performed nanosecond transient absorption measurements for compound **2** in toluene and CH_2Cl_2 but no transient signal was detected. This result dismisses the formation of long-living species as the triplet excited states.

Figure 2. Normalized absorbance (dashed lines) and emission (solid lines) spectra of **2** in toluene (purple lines) and as a thin film (blue lines) prepared with the spin-coating method from a toluene solution. $\lambda_{\text{exc}} = 400$ nm.

Thin films of **2** (300 nm thickness) were also fabricated using the spin-coating method from solutions in four different solvents (cyclohexane, CH_2Cl_2 , toluene and acetonitrile). Figure S5 displays the normalized absorption spectra showing minor differences among the four employed solvents. The comparison with the absorption spectra in solution (Figure 2) reveals a minor red-shift of the two absorption peaks in the solid state samples together with a change in the relative intensity of the peaks (most outspoken for films obtained from a solution in cyclohexane). In addition to this, Figure S5 discloses that the normalized emission spectra of **2** in the thin films are basically the same regardless of the deposition solvent with the maximum emission at $\lambda_{\text{max}} = 500$ nm, corresponding to the emission spectrum in a non-polar solvent (Figure S3). Furthermore, the position and shape of the emission spectra in the solid state (see Figure 2 and S5) are comparable to those obtained in the extreme polarity solvents, cyclohexane and acetonitrile. Importantly, the fluorescence quantum yield was measured giving the same

value $\Phi_f \approx 0.27$ for all samples. For all films, independent of the coating solvent, a bi-exponential fluorescence decay with decay times in the range 2.12 to 2.42 ns and 7.21 to 7.90 ns is observed (Table S2). The slow decaying component contributes most to the stationary emission and its decay time is in the same range as the decay times of the slow decaying component in a solution in cyclohexane or acetonitrile. The relatively long lifetimes are consistent with the high quantum yields found in the films ($\Phi_f \approx 0.27$). All results clearly indicate that the same particular species is formed during the deposition of **2** as a thin film regardless of the solvent. Although, the assignment of the type of species responsible for the emission signals in the thin films is not straightforward the result suggest that it resembles the aggregates formed in the cyclohexane and acetonitrile solvents.

To shed light into the type of emissive species in the solvents with low solubility of **2** and in the thin films, the emission spectra of **2** in THF upon addition of growing amount of H₂O were measured (Figure 3A). The intensity of the fluorescence signal drops to a 1% of the initial value when adding only 10% H₂O because of deactivation following the ICT process. However, at a 70% of H₂O in the mixture, the fluorescence signal is recovered to $\sim 600\%$ of the initial one in neat THF (Figure 3B). The latter behavior is generally attributed to the formation of aggregates taking into account the extremely low solubility of **2** in H₂O.

Figure 3. (A) Emission spectra of **2** in THF/H₂O mixtures. (B) Variation of the emission intensity of **2** in THF/H₂O mixtures at $\lambda_{em} = 525$ nm. $\lambda_{exc} = 415$ nm.

The enhanced fluorescence quantum yield with respect to the **2** monomer in polar solvents, resembles the so-called aggregation-induced emission (AIE) phenomenon.⁵ The molecules with AIE properties typically possess intramolecular

rotors in their structure, as for example the triphenylamine moiety in molecule **2**.¹³ Interestingly, the emission spectrum of the AIE of aggregates of **2** resembles very well to that of **2** in the thin films, considering position of the absorption maximum and emission and features of the spectrum. We therefore suggest that the emission signal in the solid state should be attributed to the formation of AIE aggregates of **2**. The fluorescence decay times of the films differ significantly from those obtained in toluene, THF or anisole solutions, which rules out the presence of monomer in the thin films and confirms the formation of the AIE aggregates.

3.4. Electroluminescence Performance.

The promising photophysical properties of compound **2** in thin spin-coated films suggest its possible use as an active emissive layer in OLED applications. According to the theoretical calculations, where the HOMO and LUMO orbitals were found at -5.3 and -2.4 eV, respectively, a double-layer light-emitting device was developed. The inset of Figure 4A schematizes the used OLED configuration: ITO anode/PEDOT:PSS (40 nm)/compound **2** spin-coated from a toluene solution (300 nm)/ 2-(4-*tert*-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole, (PBD) (20 nm)/ Al metal cathode (150 nm), where the PEDOT:PSS and PBD act as a hole and electron injection layer, respectively (see experimental Section for more information). The current density-voltage (I-V) curve of the device depicted in Figure 4A shows a typical diode behavior with a turn-on voltage of 3 V.¹⁷ The luminance is also depicted in Figure 4A with a value close to 1 Cd·m⁻² at 8 V. Figure 4B shows a color picture taken at 10 V (inset), and the electroluminescence (EL) spectrum at different driving voltages of the same device.

Figure 4. (A) Current density-voltage (I-V) and luminance curves, and (B) Electroluminescence spectra of the prepared OLED. The inset in Figure A shows a schematic representation of the energy-levels of the materials used in the OLED. The inset in Figure B shows a photograph of the device under 10 V.

A broad EL spectrum, from 400 nm to 700 nm with a maximum around 500 nm was obtained, which becomes more intense, slightly broader (from ~ 3300 to 3400 cm^{-1}) and with the maximum wavelength shifting from 500 to 520 nm upon increasing the forward bias (see Figure S6). The reason behind all these new features is the involvement of two emitting species peaking at ~ 460 nm and ~ 560 nm upon increasing the driving voltages. These species could be related to the presence of exciplexes and/or electropoles in the bi-layer devices, as it has been previously reported.^{18-20,21} On one hand, the exciplex emission can be estimated using the following equation:²²

$$h\nu_E = E_{D^+/D^-} - E_{A/A^-} - 0.15\text{ eV } (\pm 0.1\text{ eV}),$$

where E_{D^+/D^-} is the oxidation potential of **2** (0.5 eV) and E_{A/A^-} is the reduction potential of PBD (-2.0 eV).²³ The obtained value of 2.6 eV (470 nm) matches well with one of the maxima of the EL spectra, which proves the presence of exciplexes in our device. On the other hand, the formation of electropole when an exciplex is observed is fairly high since the minimum distance needed to form an electropole is larger (0.4 – 0.7 nm) than that required for the exciplex emission (0.3 – 0.4 nm).²⁴ Moreover, the electropole emission is normally red shifted compared to the exciplex due to the extra electron-hole stabilization in the HOMO and LUMO orbitals of each molecule that form the bimolecular complex.¹⁰ This additional stabilization is due to the distribution of electron and hole levels in amorphous materials.^{21, 25} Based on the previous facts, the red emitting species around 560 nm could be assigned to the electropole emission.²⁶ Remarkably, a similar phenomenon has been observed for similar bipolar molecules using the same double-layer device architecture.^{8,9} Although in that example the main EL mechanism was based on electromers, excimers or exciplexes,^{8, 9} in our case the presence of a better acceptor group in **2** decreases the formation of electropole and electromer in favor of the electron-hole recombination in the HOMO-LUMO orbitals of the molecule.

To validate our assumption, single carrier devices were fabricated to characterize the electron and hole mobility. For “hole only” devices an ITO/PEDOT:PSS anode and a Ag cathode (-4.8 eV) was used, meanwhile, for the “electron only” device, an Yb anode and PBD/Al cathode were employed. In this way, the electron carrier and hole carrier were respectively blocked in each device by mismatching the energy alignment between the electroluminescent material and the work functions of the contacts. Figure 5A shows that the current density is much lower than in the normal OLED configuration (Figure 4A) and no EL was observed, which confirms that only a single carrier is present in these devices. From the log-log plot of the I-V curve (Figure 5B) it could be extracted that two regimes are present: 1) ohmic current (below 5 V, slope ~ 1) and 2) space charge limited current (below 5 V, slope is ~ 2.1). From the last one, where the current is “bulk limited”, the Child’s law (Equation

1)²⁷ can be applied to estimate the electron and hole mobility in the emissive layer.

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3}$$

where J is the current density, ϵ is the permittivity, μ is the mobility, d is thickness of the EM layer and V is applied voltage.

Figure 5. Current versus voltage (I-V) curve for single-carrier devices (electron and hole devices) (A) linear plot and (B) log-log plot where the blue and green lines represented the linear fits for the Ohmic and space charge limited current (SCLC), respectively.

According to that, the electron and hole mobility for **2** are 2.94 and $5.40 \times 10^{-6}\text{ cm}^2\text{ V}^{-1}$, respectively. The results confirm that the presence of better acceptor groups in the azaindole core, enhances the electron mobility by one order of magnitude leading to a better charge balance as compared to other azaindole based devices.⁹ Therefore, the probability that the radiative recombination occurs in the EM layer instead of in the interfacial region between EM and injecting/transporting layers is enhanced. The efficacy of the prepared OLED was also determined as the ratio of the light emission versus current density.²⁸ In this case, considering the light emission as the electroluminescent intensity (as it has been reported previously),⁹ the obtained value reaches $160000\text{ counts}\cdot\text{s}\cdot\text{A}^{-1}$

(almost 2 orders of magnitude higher than using other azaindole molecules).⁹ Moreover, the absolute external quantum efficiency (EQE) was also measured obtaining a value of $6.5 \cdot 10^{-5}$ at 8 V, a low value but in a non-optimized device. It is worth to note that the main aim of this study is to demonstrate the importance of the molecular design in the performance of the OLED devices.

4. Conclusions

In summary, a thermally stable donor-acceptor luminescent derivative based on azaindole with AIE phenomenon is synthesized and characterized. The emission spectra in solvents with moderate polarity reveal a reduction of the emission intensity and a bathochromic shift of the maximum of the emission upon increasing the polarity of the solvents. This behavior is ascribed to the presence of a non-radiative deactivation process via a conical intersection involving a twisting of a single bond followed by a complete charge separation between the donor and acceptor units, an intramolecular charge transfer (ICT) process. A double-layer light-emitting device was developed showing that the presence of a stronger acceptor group in the azaindole core, enhances the electron mobility by one order of magnitude leading to a better charge balance as compared to other azaindole based devices. These results point out the importance of the rational molecular design of the simple emissive material for a better performance of the OLED devices and the future potential applicability of this new compound as electroluminescent material for non-doped OLEDs.

Conflicts of interest

Dr. E. M. Garcia-Frutos has equity ownership in a company which is developing products related to the research here reported.

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