

Uses of Self-assembled peptide structures doped with electroluminescent compounds

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ABSTRACT

A wide range of supramolecular nanostructures can be obtained by diverse materials. Capabilities inherent of supramolecular systems are used in attempt to promote controlled self-assembly processes by controlling characteristics of the environment in which they are produced. The interest on doping these structures with a variety of additives lies in the possibility of incrementing their already surprising properties. This work aims to produce distinct Phe-Phe self-assembled structures combined to electroluminescent compounds, in order to obtain new charge transfer complexes for applications such as sensors and solar cells. Produced materials are characterized by steady state and time resolved fluorescence spectroscopy, Electronic scanning microscopy and computational calculations.

Keywords: diphenylalanine, 9-vinyl-carbazole, poly-vinyl-carbazole, Time resolved fluorescence.

1 INTRODUCTION

A wide range of nanostructures can be obtained by diverse materials, since simple inorganic compounds to organic systems [1]. Among the most common approach employed to obtain supramolecular materials, bottom-up strategies, based on direct synthesis of nanoparticles, are preferred by scientists, once they enable particle size and shape control by modulating the preparation conditions [1,2]. Capabilities inherent of supramolecular systems are used in attempt to promote self-assembling processes to result in these structures, by controlling determined characteristics of the environment in which they are produced [3]. Also, supramolecular chemistry approaches enable the understanding of formation processes and associated inter and intramolecular forces that influences the material organization into new structures and, based on that, to modulate the experimental conditions and procedures in order to achieve the desired structures [4].

Among the most prominent nanomaterials that find applications in science and technology are sp^2 carbon-based structures, which can be prepared presenting distinct morphologies and peculiar properties[5-6]. Those properties raises the question on whether other organic compounds could present similar behaviors when self-assembled into these structures? After Ghadiri et al. [7a,b] has reported in 1993 the synthesis of peptide nanotubes, in which different peptides assume a bi-dimensional ring form, with lateral chains packed in an anti-parallel way and interacting to each other to give a beta-sheet structure, the

interest for L-L-Diphenylalanine (Phe-Phe) became instantaneous. Although several peptides have been employed to describe the forces involved in self-assembling processes [8], the interest devoted to FF is due to its ability to self-assemble into distinct structures, depending on the experimental procedures adopted and the unique properties presented by each structure. Regarding to it, Reches and Gazit [9] showed that Phe-Phe and derivatives self-assemble in water to form nanotubes. Also Gorbitz [10] showed, by X-ray diffraction, that Phe-Phe nanotubes present a hexagonal organization in which the inner channels are hydrophilic, while the external portion is hydrophobic.

The interest on doping these structures with a variety of additives lies in the possibility of incrementing their already surprising properties and supply the needs of industry and science for new materials. Carbazole derivatives are fascinating compounds due to their ability of forming charge transfer complexes when associated to other electron-carriers. Their polymerization has provided new and efficient compounds for application in electroluminescent devices and sensors. Recently, Promarak te al. [11] produced a series of green-emitting dendrimers based on a coumarin core, with carbazole dendrons incorporated to it and they reported reduced crystallization of the system with high emissive ability retention and, additionally, a thermal stability enhancement. Also, Grigalevicius et al. [12] produced polystyrenes containing electronically isolated carbazole, among others, and proposed them as hosts for OLEDs of high thermal stability, while Liao et al. [13] synthesized new carbazole derivatives with high glass transition temperatures and showing the right triplet energies to be employed as host materials for blue phosphorescent organic light emitting diodes (PHOLEDs) along with Iridium derivatives.

The combination of two different charge carriers with distinct characteristics is thought on the development of white devices, such as reported by Li et al.[14], in which a p-poly(9-vinyl-carbazole)/n-ZnO nanorods (NRs)/p-MEH-PPV dual heterojunction is presented as white light-emitting diode for instance.

1.1 Photophysical processes

There are several ways on a given excited state specie can transfer energy to other on fundamental state, which can be grouped on radiative and non-radiative mechanisms. Efficiency for each mechanism is a function mainly on distance between interacting species. Electroluminescent

polymers can emit with high efficiency and uniformity [15]. The emission wavelength depends on the energy difference between π - π^* states, which is consequence of factors like chemical structure (that defines emission region once influences energy levels); conjugations length (the increment of conjugations into a cromophore directs emission spectra to upper wavelengths); and concentration (once aggregattes are observed, non radiative mechanisms tends to happen, directing spctera also to upper wavelengths [16].

Two processes of non radiative mechanisms can be cited. Förster, related to dipole-dipole interactions on long distances, and Dexter's mechanism, related to electron transfer on short distances. Förster's mechanism enunciates a first step on which a Donor cromophore (D) is excited by one photon absorption (D^*). As the electron is excited from LUMO to HOMO, dipole moment is changed. Interaction between D^* and A is proportional to electric dipole moment and inverse to the distance. In this work Förster mechanism is applied to explain data[16]. Singlet fission is a process defined as an organic cromophore into excited state shares its energy with a neighbor into fundamental state, and both are converted to triplet states with half of energy. Singlet fission can't be considered a common intersystem cross, due to dipole-dipole interaction and spin-orbit coupling.

2 OBJECTIVES

This work aims to produce distinct Phe-Phe self-assembled structures combined to electroluminescent compounds, via supramolecular bottom-up methodologies, in order to obtain new charge transfer complexes for applications such as sensors and solar cells.

Photophysical and morphological characterization of the final systems were carried out by Steady-State and Time-resolved Fluorescence Spectroscopy, Scanning Electron Microscopy (SEM). Theoretical calculations were used to inform about the low energy structural configurations of Phe-Phe self-assembled structures, and from the combined analysis of such results, information on the delicate balance of forces that favor the formation of a specific structure s, as well as, on the charge transfer complex formation between were obtained.

3 EXPERIMENTAL

Diphenylalanine (Sigma-Aldrich) self-assembled structures, pure and doped, with 9-vinyl-carbazole (9Cz) (98% pure, Sigma-Aldrich) and poly-(9-vinyl-carbazole) (PVK - ADS), were prepared in Eppendorfs flasks and glass substrates, from previously prepared Phe-Phe and additives solutions. Detailed preparation protocols are presented below.

PhePhe solution: A solution with 2,5mg/mL of Phe-Phe was prepared by dissolution of 0,53mg/mL of Phe-Phe into 200 μ L of 1,1,1,3,3,3- hexafluoropropanol (HFP) (Aldrich).

9Cz solution: 10 mL of 9Cz solution at the concentration of 10^{-4} mol L^{-1} is prepared by dissolution of

the correct mass in tetrahydrofuran (THF) (Tedia, spectroscopic grade), then diluted to 10^{-6} mol L^{-1} .

PVK solution: is prepared by dissolution of 0,0012g of PVK (ADS American Dyes Source) in tetrahydrofuran (THF) (Tedia, spectroscopic grade) and diluted to 10^{-8} g L^{-1} .

PhePhe structures produced in THF: 10 μ L of the previously prepared solution was placed over a glass substrate together with 10 μ L of THF. The glass substrate was placed in an oven at 45 °C for 30 min to solvent removal and stored in a sealed Petri dish under refrigeration (2D-self assembly). Simultaneously, 200 μ L of THF was added to the Eppendorf flask containing the Phe-Phe solution and it was also stored under refrigeration(3D-self assembly)

PhePhe structures produced in THF with 9Cz as doping agent: 2D self-assembly was performed for this mixture exchanging THF for 9-vinyl-carbazole solution in THF. 3D self-assembly follows the same change.

PhePhe structures produced in THF with PVK as doping agent: 2D self-assembly was performed for this mixture exchanging THF for PVK solution in THF. 3D self-assembly follows the same change.

3.1 Characterization

Scanning Electronic micrographs were recorded in a SEM Jeol, JSM-6610 microscope, coupled to EDS Thermo scientific NSS Spectral Imaging. A Denton Vacuum, Desk V was used for gold layer deposition. Excitation and fluorescence spectra were recorded in a Fluorolog 3-221 Horiba Jobin Yvon spectrophotometer, with a 450 W Xe arc-lamp, connected to a double monochromator, polarization system in the entrance . Emission was detected at 90° by a Hamamatsu photomultiplier, operating at the range of 250 to 850 nm. Narrow slits were employed to guarantee the resolution of 1.0 nm to the measurements. Lifetimes measurements were recorded in a FluoroHUB-A TCSPC module with LED emission in 345 nm coupled to Fluorolog 3-221 spectrophotometer, and emission observed at 360nm.

4 RESULTS AND DISCUSSION

Images for the resulting structures of PhePhe self assembly in THF, pure and doped, with carbazole derivatives are shown in Figure 1.

Figure 1-A shows pure self assembly PhePhe structures in THF. The image shows lamelar structures with 2-10nm length but, no evidence of nanotubes formation is observed. The occurrence of that kind of lamelar structure is in concordance to the theory of initial formation of β -sheet as suggested by literature. those observations are based on rare 2D structures observed on substract limits (not shown). In center of substract we believe 3D assembly can rises and aggregattes are formed by packing sheets, as shown in Figure 1-A. Figure 1-B shows 9Cz doped self assembly Phe-Phe structures obtained. Hexagonal geometry is observed as for Phe-Phe nanotubes.

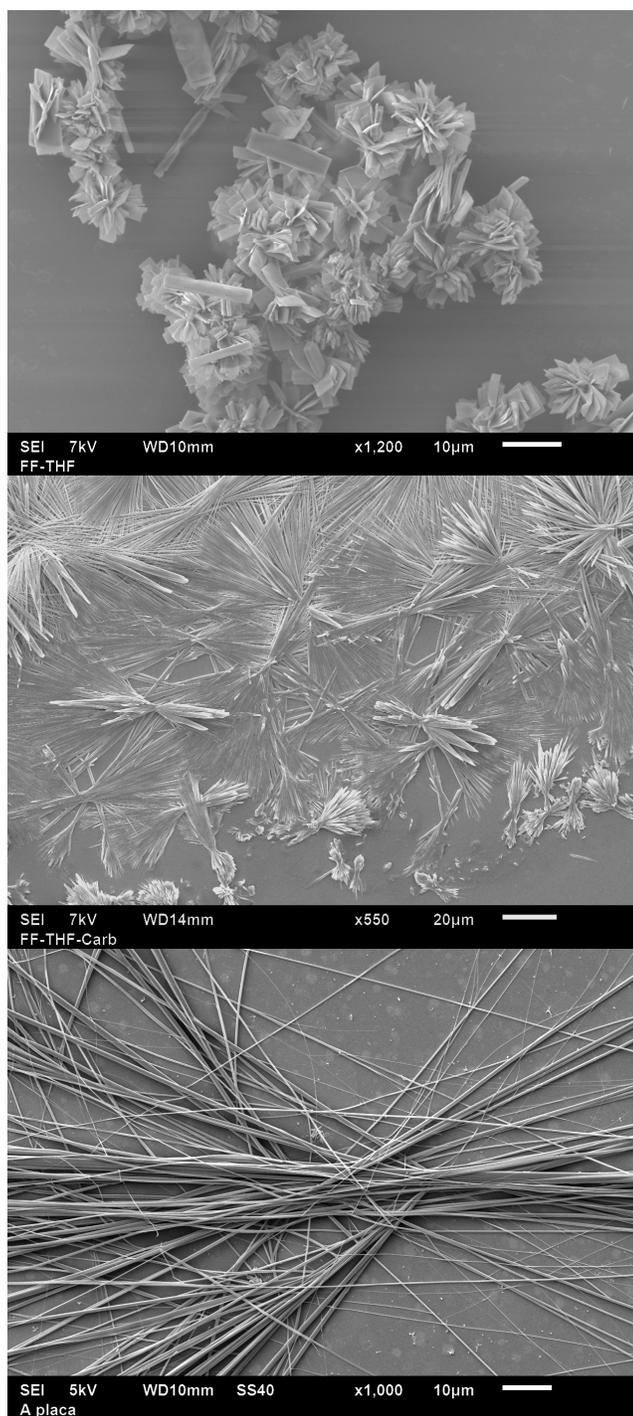


Figure 1: MEV for self assembly PhePhe structures in (A) THF, (B) 9Cz solution in THF, (C) PVK solution in THF.

According to Gorbitz [10], this is the pure PhePhe geometry organization, that implies, on our work, that these structures doesn't contain inserted 9Cz onto it's structure. Oterhwise, rare β -sheets occurrences at substrate limits can be observed. This fact bring us to affirm that these sheets serve as seeds to the growing of more complex nanostructures. PhePhe and 9Cz molecules can interact positively influencing Pi interactions directing self

assembly to nanotubes. Also 9Cz molecules can be found inside NTs due its solubility on THF associated to hidrogen interactions onto NTs hydrophylic protons.

Figure 1-C shows PVK doped self assembly Phe-Phe structures obtained. This structure is slightly different from obtained of previous figure. One can realize long nanowires not growing from seeds (well defined regions), and not interacting when colliding, that indicates chain length effctcs, like a coating effect onto nanotubes. Also is possible to perceive nanotubes aggregation to microtubes (data not show). Fluorescence spectra were obtained for all materials and results are shown on Figure 2.

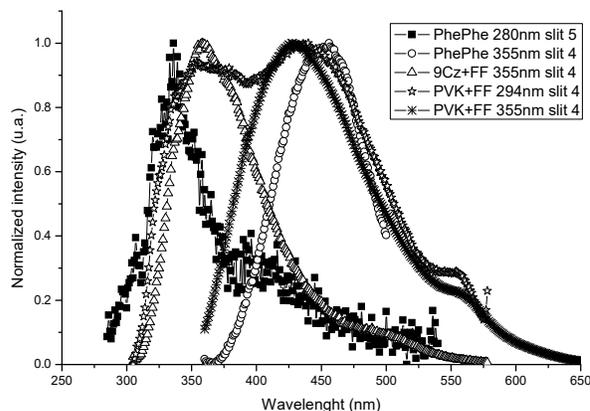


Figure 2: Fluorescence spectra for different structures obtained.

Fluorescence spectra were obtained to self assembly Phe-Phe at 280nm and 355nm. Excitation at 280 nm shows maximum at 335nm with a half-width shoulder at 360 nm partially covered by a band at 410 nm. Fluorescence spectra at 360 nm shows only a band at 455 nm. Self assembly 9Cz-PhePhe material fluorescense spectre, when compared to 9Cz isolated spectra (data not shown), looks structured and red-shifted with maximum around 415 nm, while expected maximum for isolated 9Cz in solution is around 361 nm. Additionally, there is a shoulder with low intensity above 500 nm that is related to excimer formation. So, 9Cz can be distributed over the NT surface on small distances, considering that the principal interaction between Phe-Phe and 9Cz is electrostatic and involves their charged terminals. The total red-shift observed for Phe-Phe /9Cz complex indicates that a charge transfer complex was formed. Fluorescence spectra obtained in 294 nm for Phe-Phe/PVK show less intense, red-shifted peaks of PhePhe, inferring on the possibility of radiative energy transfer between PhePhe and PVK. The band with maximum observed at 355 nm is much similar to 9Cz.

Fluorescence lifetime decay can inform about the distinct species that contribute, into a given wavelenght, to the stationary spectrum. TCSPC experiments were carried out for all samples. Pure self-assembled Phe-Phe solution shows a fitted mono-exponential decay with $\tau=2,6070$ ns, indicating that only one cromophore is contributing to the total decay curve. At this spectral region there are no

isolated molecules emitting, and the observed emission must come from aggregates. To the self-assembled system containing 9Cz, fluorescence decay shows a bi-exponential behavior with lifetimes $\tau_1=0,5591$ ns and $\tau_2=0,8695$ ns. Multi-exponential decays occur for multi entities contributing to the total decay curve, and, in this system, formed of peptides and conjugated polymers, short decay times are due to conjugated polymers. To the PVK system, the observed behavior is also bi-exponential with lifetimes $\tau_1=2,5930$ ns and $\tau_2=0,7980$ ns. Also interesting, this system shows one cromophore with lifetime very similar to that observed for self assembled Phe-Phe, and another cromophore very similar to 9Cz systems. The clear relation between nanostructures and eletroluminescent species that influences photophysical behavior is showed.

In order to obtain information about possible singlet fission processes, computational calculations were carried out first optimizing 9Cz and PVK structures using AM1 model with THF as implicit solvent, and second calculating vertical energy of excitation to the first twenty excited states for 9Cz and PVK using ZINDO/S. The results are condensed into Figure 3. The results suggests that to PVK, singlet fission processes, if any, can theoretically occur from first singlet state (18th) state, around 3,6 eV, to triplet states around 1,8 eV. To 9Cz, results shows that the first singlet state is around 3,85 eV, but no triplet state is found at 1,9 eV, suggesting that singlet fission is more difficult to occur on 9Cz system.

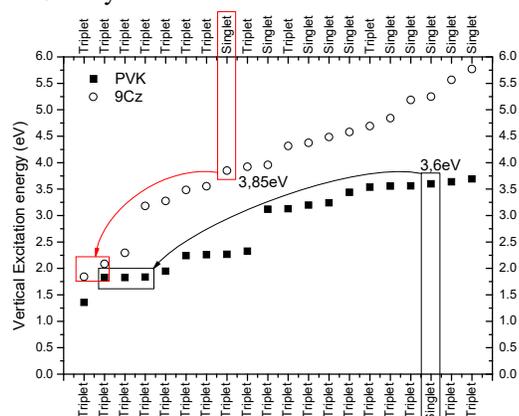


Figure 3: Calculated first twenty excited states for 9Cz and PVK where singlet fission processes can occur.

5 CONCLUSIONS

Phe-Phe self-assembling is governed by preparation conditions. Additives with distinct characteristics such as electron donor/acceptors or polymeric/small conjugated molecules interfere in nanostructures mechanism of interaction raising distinct structures. Fluorescence results, shows distinct behavior when compared to the optical response of the isolated precursors. Spectra recorded for 9Cz and PKV system are very similar spectrum, as well as the lifetime fluorescence results. Domain investigations also corroborates, once it shows multi-exponential behaviors for both systems (9Cz and PVK) with

comparable lifetimes for cromophores, suggesting that all systems shares similarities on its chromophores.

Computational simulations shows a first singlet state with characteristics of a intercrossing system, and also triplets states with aproximately half of singlet state energy were found in these systems. suggesting exciton fissions processes are possible once it is an intrinsic property of these molecules. Steady state and time resolved fluorescences indicates that different structures of self assembled PhePhe can modulate the energy gap, and in theory, positively influence its occurrence.

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