Solvent effects and energy transfer processes in luminescent composite

Alessandra S. Menandro (Writing - original draft), Leonardo J.A. Siqueira (Software), Hueder P.M. Oliveira (Methodology), Laura O. Péres (Supervision) (Funding acquisition) (Writing - review and editing)

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Solvent effects and energy transfer processes in luminescent composite

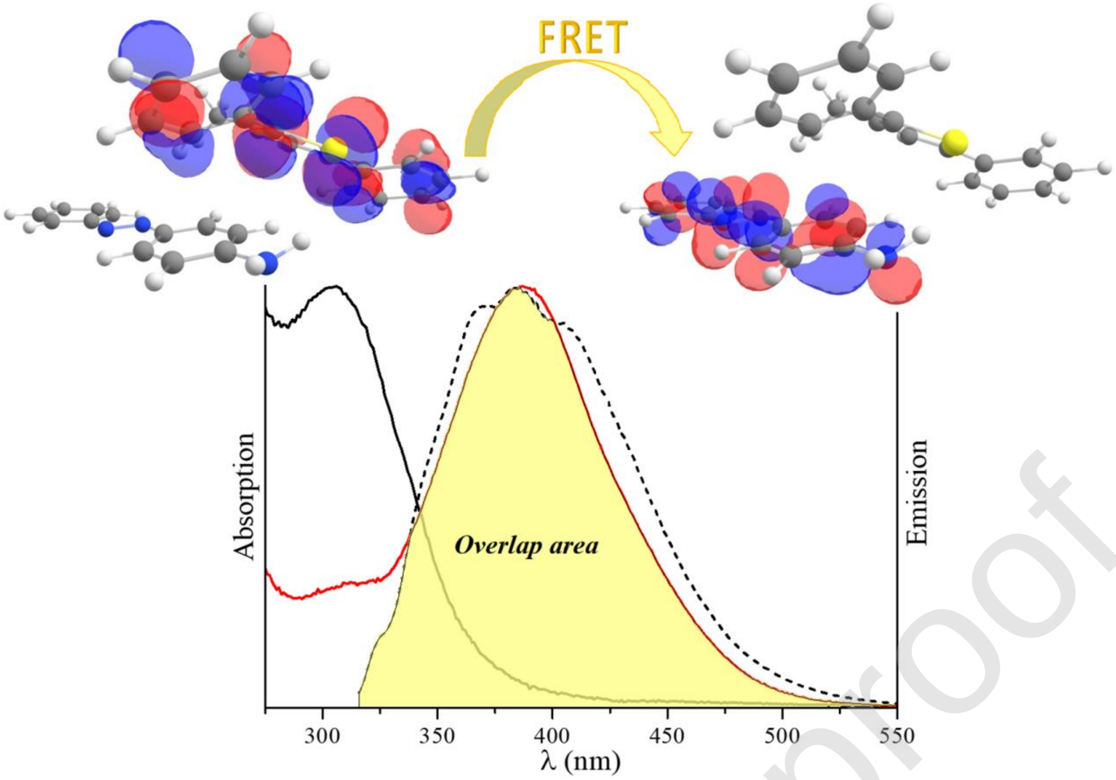
Alessandra S. Menandro[1], Leonardo J. A. Siqueira[1], Hueder P. M. Oliveira[2], Laura O. Péres[1,*]

[1] *Laboratory of Hybrid Materials, Federal University of São Paulo, SP, Brazil*

[2] *Center for Natural and Human Sciences, Federal University of ABC, Brazil*

*laura.peres@unifesp.br

Graphical Abstract



HIGHLIGHTS

- Luminescent composite formed by conjugated polymer and azocompound;
- Four organic solvents were used to understand the energy transfer process;
- Emission spectra show suppression of PTPh due to Föster's energy transfer from PTPh to Azo.
- Computational results suggest that Azo receive energy from the polymer;

Abstract

The combination of conjugated polymers and photochromic molecules can result in a composite, which can yield a new photoresponsive material. The efficiency of these materials is due to the process of energy transfer. In this work, the conjugated polymer poly (3-hexylthiophene-co-1,4-phenylene) (PTPh) was synthesized by Suzuki route and the photochromic molecule 4-aminoazobenzene (Azo), synthesized by diazonium salt coupling, were mixed forming a luminescent composite. This new material was obtained in four different solvents, in order to evaluate its influence. When the Azo is added in a solution of PTPh, it was observed a decrease of the emission spectra of the copolymer, indicating the suppression of PTPh due to Föster's energy transfer from PTPh to Azo. The larger energy transfer has been found in ethanol. Density Functional Theory (DFT) calculations have been performed for Azo, an oligomeric model for the PTPh and a complex formed by the Azo and the oligomeric model for PTPh, with two different functionals. Computational results indicate the occurrence of C-H---π and N-H---S interactions in the optimized structure of PTPh/Azo complex. The LUMO orbital of the PTPh/Azo complex is mainly located in the Azo moiety, suggesting that Azo might receive energy from the polymer. Therefore, the joint computational-experimental study enables the understanding of the energy transfer that takes place in the PTPh/Azo systems.

Keywords: conjugated polymer, azocompound, FRET.

Introduction

Photochromism can been defined as the generation of color under the influence of light [1]. Thus, the photochromic molecules have the capability of change reversibly their properties induced for an electromagnetic radiation [2–5]. These fascinating characteristics have been exploited for sensors, optical materials, polymer films and materials, optical memories, switches, liquid crystals and ophthalmic lenses [6–12]. In this context, 4-aminoazobenzene is an important photochromic molecule, which has a conjugated structure and exists in *trans* and *cis* conformation. The *trans*→*cis* isomerization occurs under irradiation of UV-visible light, whereas the *cis*→*trans* isomerization occurs spontaneously when the light is removed in accordance with higher thermodynamics stability of the latter. [6,13,14].

Conjugated polymers are macromolecules that have alternate sequence of single and double bonds (delocalized electrons). The great interest in conjugated polymers has increased because of their ability to be use as diodes, displays, sensors, optoelectronic and electronic devices [15–19]. The copolymer containing thiophene group is a versatile material that can emit light in distinct wavelengths of the spectrum. Additionally, when phenylene group are present, the copolymer remains luminescent and the emission spectrum is blue-shift, which is useful for several applications in optoelectronic devices [20,21].

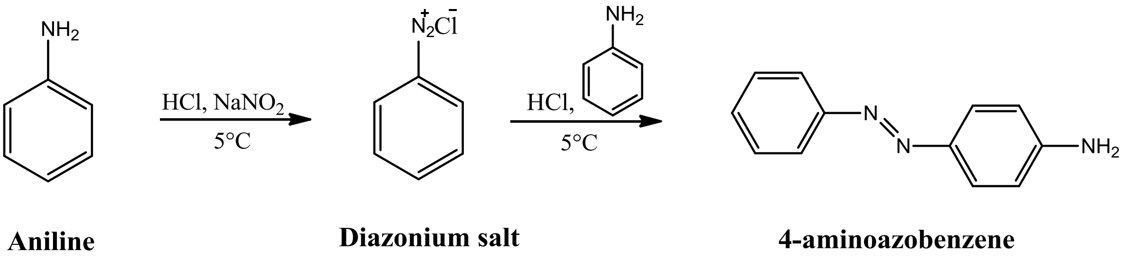
Composites formed by photochromic molecules and conjugated polymers can yield new photoresponsive materials [1,3,22]. The efficiency of these materials is related to the photophysics process of energy transfer, which occurs between the photochromic molecules and the polymers with modulation of fluorescence. The energy transfer process occurs when the donor fluorophore (in this work - the copolymer) absorbs the energy from the excitation and transfer to the acceptor (chromophore - azo) that can emit [3,23]. There are few criteria that must be satisfied to occur the energy transfer process: i) the emission spectrum of the donor must overlaps the absorption spectra of the acceptor; ii) the absorption bands of the donor and acceptor must be spectrally separated and; iii) the fluorescence lifetime of the donor must be long enough to allow the occurrence of the process. [3,23,24] .

Some studies involving the process of a photochromic molecule and a conjugated polymer have been already reported [3,22,24–27]. However, to the best of our knowledge, there is not any study involving azobenzene and a copolymer containing thiophene group and solvent effect to the energy transfer process in literature yet. Therefore, in this work we have studied experimentally the composite comprised by PTPh/Azo in different solvents together with DFT calculations in order to understand the energy transfer taking place in the systems, which it is of great importance for their possible application in the future as new photoresponsive materials.

Experimental Procedure

Synthesis of 4-aminoazobenzene (Azo)

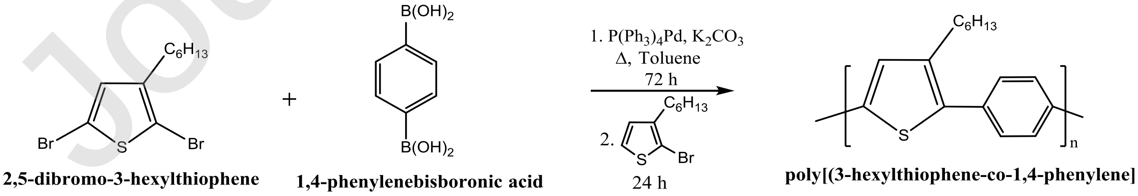
The 4-aminoazobenzene was synthetized by diazonium salt coupling according to the published procedure [28–30] (***Scheme 1***). For this, a require amount of aniline was add in HCl, and with aqueous solution of sodium nitrite, a diazonium salt solution was obtained. The coupling solution was prepared by treating aniline with HCl, followed by the addition of diazonium salt solution, where after 3h a yellow-orange precipitate of azo compound was obtained by the addition of ammonia solution. Yield: 40%. ^{1}H NMR (300 MHz, Chloroform-d, δppm): 6.73 (s, NH_2), 7.35-7.57 (m, 2H), 7.75-8.03 (m, 7H). FTIR (KBr, cm^{-1}): 3479 ($N\text{-}H_{\text{stretch ass.}}$), 3383 ($N\text{-}H_{\text{stretch sim.}}$), 3063 and 3034 ($C\text{-}H_{\text{arom. stretch}}$), 1596 ($C{=}C_{\text{arom. stretch}}$), 1418 ($N{=}N_{\text{stretch}}$), 1302 and 1240 ($C\text{-}N_{\text{stretch}}$). The detailed procedure for 4-aminoazobenzene synthesis can be found in supporting information.



Scheme 1 – *Synthetic route for 4-aminoazobenzene (Azo).*

Synthesis of poly(3-hexyltiophene-co-9,9-dioctyl-2,7-fluorene) (PTPh)

The poly(3-hexyltiophene-co-1,4-phenylene) (PTPh) was synthesized by Suzuki route [31–33] using Pd as a catalyst. The boronic and halogenic material were used in order to form the desired polymer (***Scheme 2***). A stoichiometric amount of monomers was added to the catalyst, and a 2 mol/L solution of K_2CO_3 and toluene was left in reflux for 72 h. The organic solution was washed with water, after that the solvent was eliminated, and the copolymer was purified using methanol as a non-solvent. Yield: 93%. RMN ^1H (300 MHz, Chloroform-d, δ ppm): 7.80-7.26 (m, 4H, Ph-H), 7.10-6.75 (m,1H, Th-H), 2.75-2.30 (m, 2H, CH_2), 1.70-1.50 (m, 2H, CH_2), 1.45-1.20 (m, 6H, CH_2), 1.00-0.80 (m, 3H, CH_3). FTIR (KBr, cm^{-1}): 3050 (C-H$_{\text{thiop. ring stretch}}$), 2927 and 2852 (C-H$_{\text{arom. stretch}}$), 1600 (C=C$_{\text{arom. stretch}}$), 1462 (C-H$_{\text{side chain bend}}$), 695 (C-S-C$_{\text{thiophene ring stretch}}$). GPC molar mass: Mw = 1.6×10^3 g mol^{-1} and Mw/Mn = 1.53 g mol^{-1}. The detailed procedure to prepare the copolymers can be found in supporting information.



Scheme 2 – Synthetic route for poly (3-hexylthiophene-co-1,4-phenylene) (PTPh).

Study of photophysics process

The study of photophysics process was carried out in four different solvents: ethanol (Synth 99.5 %), chloroform (Aldrich 99.9 %), dichloromethane (Tedia 99.9 %) and acetonitrile (Tedia 99.9 %), and for each, it was added different quantities of the Azo solution ($6.4.10^{-6}$ g/mL) in the PTPh solution ($2.1.10^{-5}$ g/mL). The composites were analyzed for UV-Vis a photolumiscence spectroscopy in each addition. Based on Föster theory [23,34] and the results obtained, the parameters were calculated by Maple 2017 subroutine (Waterloo Maple Inc.).

Density functional Theory calculations

All the density functional theory (DFT) calculations were performed with the Gaussian09 suite program [35]. Preliminary calculations of molecular geometry optimization of Azo and PTPh model were done with the B3LYP/6-31+G* level. Starting with the previous optimized structures, the Azo, PTPh model and complex PTPh/Azo have their optimized structure obtained by different levels: B3LYP [36] and M062X [37] functional with 6-31+G (d) and 6-311+G (d) basis set, and in environment of ethanol and vacuum. For all complexes the interaction energies were calculated based on the obtained electronic structures and for structures optimized in vacuum. The standard counterpoise correction was applied to eliminate the basis set superposition error (BSSE). The absorption spectrum, oscillator strengths and orbitals HOMO and LUMO were computed at the TD-DFT level with the B3LYP functional and the 6-311+G (d) basis set.

Characterization

The PTPh and Azo was characterized by NMR, infrared spectroscopy, UV-Vis and photoluminescence spectroscopy. For NMR a Bruker Ultrashield 300 spectrometer operating at 300 MHz were used for ^{1}H, and deuterated chloroform – $CDCl_3$ (Aldrich

99.8% D + 0.03% TMS) was used as a solvent. The infrared spectra were obtained using a Shimadzu IRPrestige-21, in the range of 4000 to 400 cm^{-1}, 256 scans, 4 cm^{-1} of resolution, using KBr in the transmittance mode. The UV-Vis measures were performed by ThermoScientific Evolution 201 spectrometer with 1 cm path length quartz cuvette. The Horiba Fluoromax-4 fluorimeter was used to emission spectra and the excitation lengths were obtained by the maximum observed in absorption spectra. A cuvette of 1 cm path length quartz was used. Gel permeation chromatography experiments (GPC) were performed using an Agilent 1100 equipment with refractive index detector. The solvent used was THF at 1 mL min^{-1} at 23 ºC and the samples. Used columns (1PLgel mixed C and 1PLgel mixed B) were calibrated using polystyrene (PS) standards.

Results and Discussion

According to the literature, the energy transfer process can occur when the emission spectrum of the PTPh overlaps the Azo absorption spectra, but the absorption bands of the PTPh and Azo must be spectrally separated, with the requirement that PTPh be efficient enough in order to allow the happening of the process[38]. These characteristics have been observed in the results obtained here and suggest that the energy transfer can occurs in this composite.

The use of different solvents can change the solute-solvent interactions and consequently, the spectra of the compounds. For each solvent, the Azo has a different absorption maximum: for chloroform at 366 nm, dichloromethane at 374 nm, ethanol at 386 nm, and acetonitrile at 381 nm. For the polymer (PTPh) on the other hand there are some differences but not so pronounced in the emission maximum: for chloroform at 393 nm, dichloromethane at 388 nm, ethanol at 383 nm, and acetonitrile at 384 nm (***Figure 1S*** – supporting information). The change in the maximum of the absorption shows a shift of the spectrum as a whole and consequently the overlap area between the emission spectrum of the PTPh and the absorption spectra of the Azo, as can be seen in the ***Figure 1***.

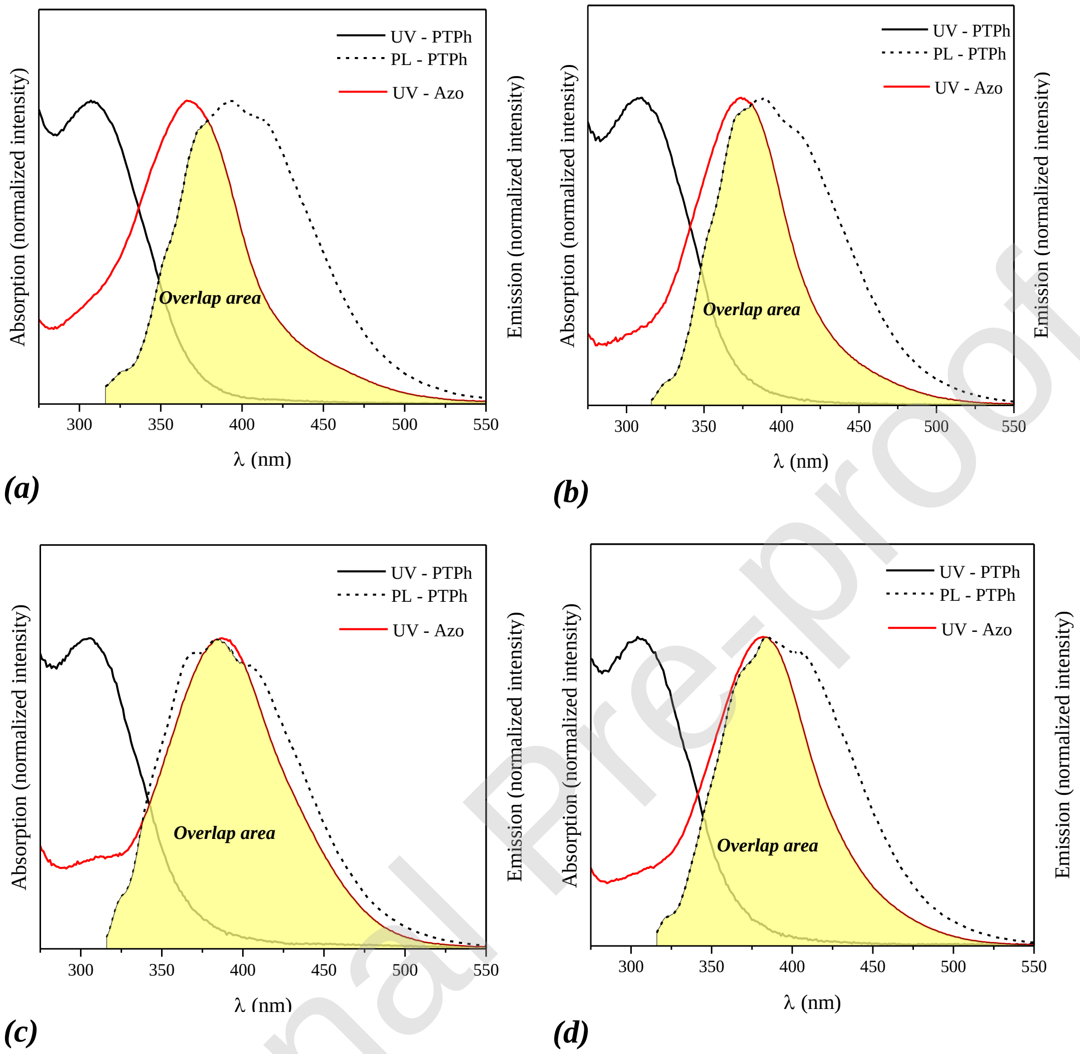


Figure 1 **–** The absorption (solid) and emission (dashed) spectra of PTPh and Azo and its respective overlap area in different solvents. ***(a)*** chloroform; ***(b)*** dichloromethane; ***(c)*** ethanol; ***(d)*** acetonitrile.

When a solution of Azo is added into a solution of PTPh, it is possible to observe a decrease of the intensity at maximum of polymer and an increase at the chromophore maximum in the absorption spectra. Besides that, it is observed an overlap between the bands and a small shift to higher wavelength of the polymer curve (***Figure 2S*** – supporting information). The emission spectra showed that upon the addition of the Azo there is a linear decrease of the maximum of PTPh luminescence intensity (***Figure 3S*** – supporting information). There is clear quenching of the polymer emition, which increases as the Azo concentration increases, indicating that the energy transfer process is occurring from PTPh to Azo, independently of the solvent (***Figure 2***).

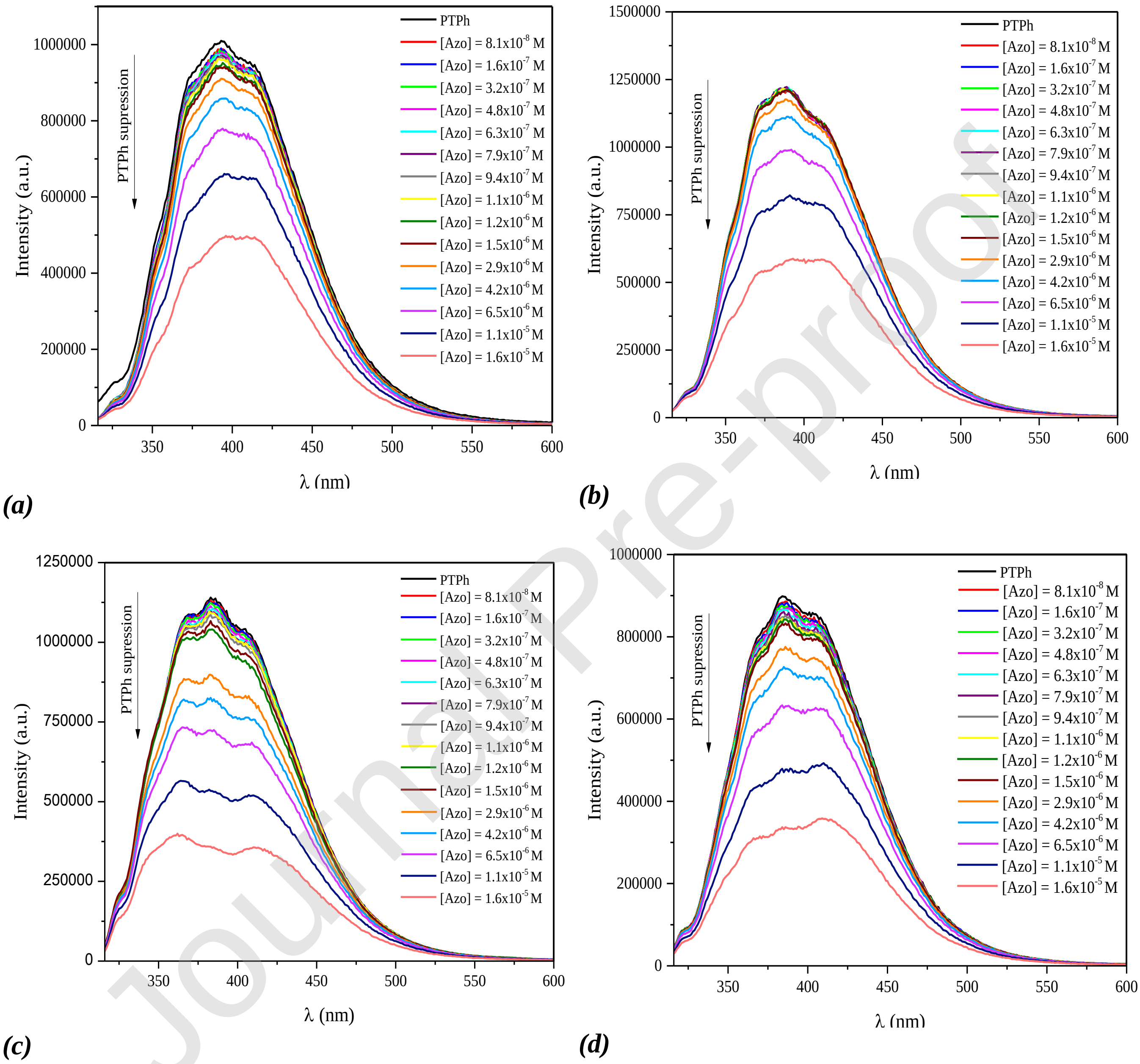


Figure 2 – Emission spectra of the addition of Azo 6.6x10^{-6} g/mL in PTPh 2.1x10^{-5} g/mL in different solvents: ***(a)*** chloroform, λ_{exc} = 307 nm; ***(b)*** dichloromethane, λ_{exc} = 310 nm; ***(c)*** ethanol, λ_{exc} = 306 nm*;* ***(d)*** acetonitrile, λ_{exc} = 304 nm.

Based on the obtained results and the theory of Förster mechanism [23,34,39,40], the parameters, like the Föster's critical radius, the acceptor critical concentration, the distance *r* between the donor and acceptor and the efficiency of energy transfer, can be calculated indicating the characteristics about each system, which the PTPh is the donor and Azo the acceptor. The efficiency (*E*) of energy transfer can be calculated by equation *(1)*,

$$E = 1 - \frac{I}{I_0} \tag{1}$$

Where *I* is the donor emission with the acceptor and I_0 is the donor emission without the acceptor.

The acceptor critical concentration (C_0) and the acceptor concentration (*C*) can be obtained by:

$$E = \pi^{1/2}\left(\frac{C}{C_0}\right) exp\left(\frac{C}{C_0}\right)^2 \left[1 - erf\left(\frac{C}{C_0}\right)\right] \tag{2}$$

The efficiency depends strongly the type of the solvent, because each one solvate in a different way in the polymeric chain and in the photochromic, altering the packing and the orientation between the PTPh and the Azo. This process also changes the efficiency of energy transfer [23,41]. The result of this process of efficiency can be seen in ***Figure 3*** in function of the relation C/C_0 for each solvent. It is observed that the efficiency of energy transfer in the composites is directly related to the overlap area of the spectra of Azo absorption and PTPh emission (***Figure 1***), so analyzing the results it is possible to confirm that for the ethanol there is the largest overlapping area and consequently the greater efficiency. These results can also be confirmed in ***Figure 3***.

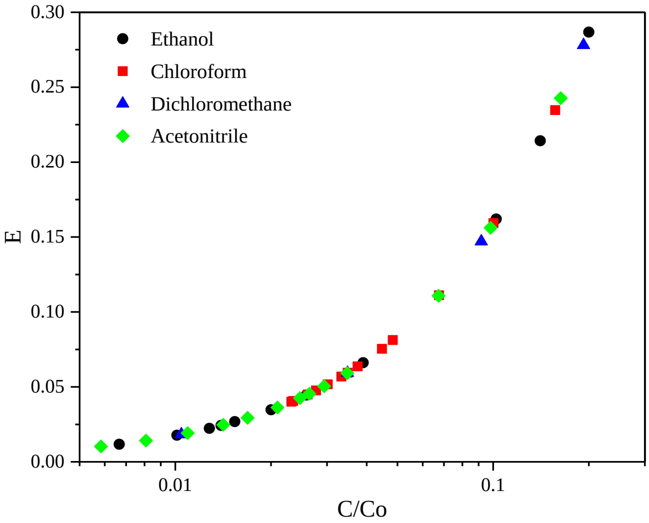


Figure 3 –Effect of the solvent to the energy transfer. *E* stands for efficiency and Log C/C$_0$ is the logarithm of the concentration ratio.

The Föster's critical radius (*R$_0$*) is the distance between the donor (PTPh) and the acceptor (Azo) where energy transfer efficiency is 50%, and this parameter can be calculate by the equation *(3)* [23,39,40]. The overlap integral (J(λ)) expresses the degree of spectral overlap between the donor emission and the acceptor absorption.

$$R_0{}^6 = \frac{9000\ (\ln 10)\ K^2 Q_D}{128\pi^5 N_a n^4} \int_0^\infty \frac{F_D(\nu)\varepsilon}{\nu^4}\, d\nu \qquad (3)$$

The efficiency (*E*) of an energy transfer process can also be described by the number of photons that the donor absorbed and transferred to the acceptor (equation *(4)*). Therefore, it is possible to calculate the distance *r* between the donor and the acceptor [23,39,40].

$$E = \frac{R_0^6}{R_0^6 + r^6} \qquad (4)$$

With this theory, the values of *R$_0$* and *r* were calculated (***Table 1***). The results has shown that composites with higher *R$_0$* values are the same one that has a greater efficiency of energy transfer process´s. Moreover, for the composite formed in ethanol, the limit that the energy transfer can occur is high and consequently the process is able to occur easier than in the other solvents. In addition, it is noted that for all cases the distance *r* is higher than R_0, indicating that the emission deactivation of the PTPh is predominant [23].

The quantum yield of the materials were obtained by the equation *(5)*, using the quinine sulfate as a reference due its known quantum yield (Q_r = 0,546) [23,42].

$$Q_D = Q_r \left(\frac{D_D}{D_r}\right)\left(\frac{n_D^2}{n_r^2}\right) \qquad (5)$$

Table 1 **–** Values of Föster's critical radius (R_0), the distance between the molecules (r) for each composite (PTPh/Azo) and the quantum yield for PTPh and Azo, in four solvents.

	Chloroform	***Dichloromethane***	***Ethanol***	***Acetonitrile***
R_0 (Å)	33.71	34.52	36.83	36.51
r (Å)	46.41	54.42	50.56	50.96
Q_{PTPh}	0.456	0.521	0.462	0.349
Q_{Azo}	0.207	0.574	0.228	0.178

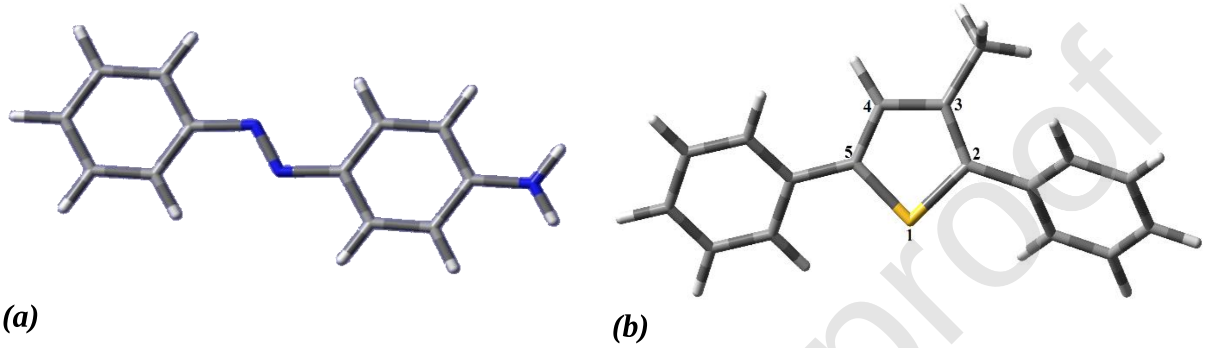
In addition to these results, the quantum emission efficiency of PTPh and Azo were calculated for each solvent (***Table 1***). For PTPh no significant differences are observed with the solvents chloroform, dichloromethane and ethanol, but it is possible to highlight the highest value for dichloromethane, probably due to the good solubility of the polymer in this solvent, resulting in the interactions solute-solvent most effective and, consequently, a better quantum yield. In addition, the emission quantum yield was also calculated for PTPh after each addition of Azo, and it shown decreasing with the higher photochromic concentration (***Table 1S*** – supporting information). In general, the Azo has lowest quantum emission efficiency than PTPh, indicating again the efficiency of the polymer as a donor and the photochromic as a suppressor in the energy transfer process.

The solubility parameters could show us how the molecules are packing inside different solvents and how it could affect the efficiency of energy transfer process once it occurs by dipole-dipole interactions. Therefore, based on the theory of Hildebrand [43] and Hansen [44], it is possible to understand these interactions between the PTPh/Azo and the solvents [41]. The values of solubility parameters for the four solvents used can be obtained in the literature [17,44,45] and is show in the ***Table 2S*** (supporting information). The literature, to the best of our knowledge, does not report the values of the PTPh, so values of similar polymer were used (poly(3-hexylthiophene)) as reference to understand the interactions of the proposed systems.

When there are a good solvent, the polymeric chains will interact more with the solvent molecules, mainly by dipole-dipole interactions and the interaction between the materials could be difficult. However, in a poor solvent, the interactions are weaker and it could possibility to increase the dipole-dipole interactions between the materials. Analyzing our systems, the solvents and the efficiency for the energy transfer process it is possible to conclude that the ethanol is a good solvent for the Azo and can interact preferentially by hydrogen bond in the NH_2 group. The parameter of the polymer reference indicates the highest solubility in chloroform (proven experimentally), the worst solvent for the energy transfer, where the interaction polymer-chloroform occur by dispersions interactions. However, the ethanol is a bad solvent for PTPh with the lowest solubility. It is interesting to observe that the solvent that allows the best energy transfer in the composite is not necessarily the one that will provide greater solubility to the materials. Based on this, it is possible to suppose that in ethanol, the polymer is coiled and the Azo is in the middle, and the interaction PTPh-Azo might be stronger than PTPh-ethanol, improving the energy transfer in the composite.

Density Functional Theory calculations

Initially, an oligomeric model for the PTPh, containing a 3-methylthiophene with two phenyl rings at the carbons 2 and 5, is proposed aiming a qualitative representation of the polymer since it has building blocks of the real polymer and it might be able to capture the most important event occurring in the real system with low computational time. Therefore, the optimized geometries of the PTPh model and the Azo obtained from B3LYP/6-31* level is presented in ***Figure 4***.



(a)

(b)

Figure 4 – Optimized geometries by B3LYP/6-31G* for ***(a)*** Azo; ***(b)*** PTPh model.

The experimental results indicate that the copolymer and Azo develop intermolecular interactions in order to have the energy transference. Therefore, we firstly optimized the structures of PTPh model with Azo in several different starting points at B3LYP/6-31G*. The complex with lowest energy (-2.315 kcal/mol) found in this screening procedure is the one that the amino group of Azo develops an unusual hydrogen bond with S of thiophene (N-H---S; *r* = 2.85 Å), ***Figure 4S*** – Supporting information.

Starting with this complex, we have performed a study of basis set, functional and solvent effects, whose results are summarized in ***Table 2***. The corresponding optimized structures are presented in ***Figure 5S*** of the supporting information.

Table 2 – Values of interaction energies and distances of the complexes calculate by different methods.

Complex	**Method**	**Energy (kcal/mol)**	**NH---S (Å)**	**CH---H (Å)**	**CH---π (Å)**	**Environment**

1	B3LYP/6-31G*	-1.518	2.84	3.07	-	Vacuum
2	B3LYP/6-311G*	-1.625	2.87	3.03	-	Vacuum
3	B3LYP/6-31G*	-1.258	2.85	3.12	-	Ethanol
4	B3LYP/6-311G*	-1.191	2.73	3.26		Ethanol
5	M062X/6-31G*	-9.465	2.81	-	2.71	Vacuum
6	M062X/6-311G*	-10.860	2.81	-	2.65	Vacuum
7	M062X/6-31G*	-7.531	2.83	-	2.61	Ethanol
8	M062X/6-311G*	-7.531	2.82	-	2.70	Ethanol

Changing the B3LYP for M062X functional, the bonding energy is remarkable increased. Such strengthening might be related to a kind of C-H---π interaction that appears only in M062X calculations that includes dispersion effects [37]. In fact, in order to check whether this CH---π like interaction occurs due to dispersion interaction, we performed a new B3LYP structure optimization starting from the complex 5. The complex with optimized structure lost the CH---π like interaction when B3LYP functional is employed. When the molecules are embedded in ethanol, their bond energies decrease in comparison with those performed in vacuum, being the larger decrease in M062X calculations.

At the electronic spectra of Azo in ethanol optimized with B3LYP/6-311G* and M062X/6-311G* there are two bands at 389 and 392 nm, respectively, which is in quite good agreement with experimental spectrum, in which there is an absorption band at 386 nm (**Figure 6S** of the supporting information). In the experimental electronic spectrum of copolymer arises a band at 306 nm, whereas in the calculated ones the absorption band appears at 321 and 326 nm for the optimized structures of PTPh model obtained by B3LYP/6-311G* and M062X/6-311G* calculations, respectively. This mismatch might be related to fact that PTPh model is not large enough the capture all the signatures of the real system. Additionally, it is important to mention that PTPh model bears only a methyl group on carbon 3 of thiophene ring, while in the real system there is a larger carbon chain (hexyl) that may promote torsion of the main chain of the copolymer. In order to check whether the side chain plays its role to the electronic spectra, we performed an additional TD-DFT (B3LYP/6-311G*) calculation with PTPh model bearing isopropyl group in the carbon 3 of thiophene ring, and it resulted in an absorption band with the maximum in 310 nm, confirming the effect of the side chain in the electronic spectra (***Figure 7S*** – supporting information).

Considering that the experimental electronic spectra were recorded using ethanol solutions of the materials, we used the complex 4 and 8 in order to calculate the electronic spectra by means of TD-DFT calculations with B3LYP/6-311G*. For both the complexes there are two absorption bands in calculated spectra around 320 and 390 nm with negligible shift in comparison with the calculated spectra of Azo and PTPh model alone in ethanol.

Figure 5 shows the energy diagram and HOMO and LUMO orbitals obtained from the TD-DFT calculations. For PTPh model and Azo structures calculated by the complexes 4 and 8, on both, the orbitals are dislocated on all conjugated structure, where HOMO are located mainly on double bonds and LUMO on the single bonds. In complex 4, the HOMO and LUMO are located on Azo, whereas HOMO-1 and LUMO+1 are located on PTPh model. However, in the case of complex 8, both Azo and PTPh model contribute to HOMO and HOMO-1, which might be related to the high bonding energy provided by NH---S and CH---π like interactions. The LUMO and LUMO+1 are located on only Azo and PTPh model, respectively.

As previously mentioned, ethanol is not a good solvent for PTPh, so that Azo might be trapped by PTPh, allowing the development of NH---S and also CH---π like interactions that might be the ones responsible for the energy transfer process observed experimentally.

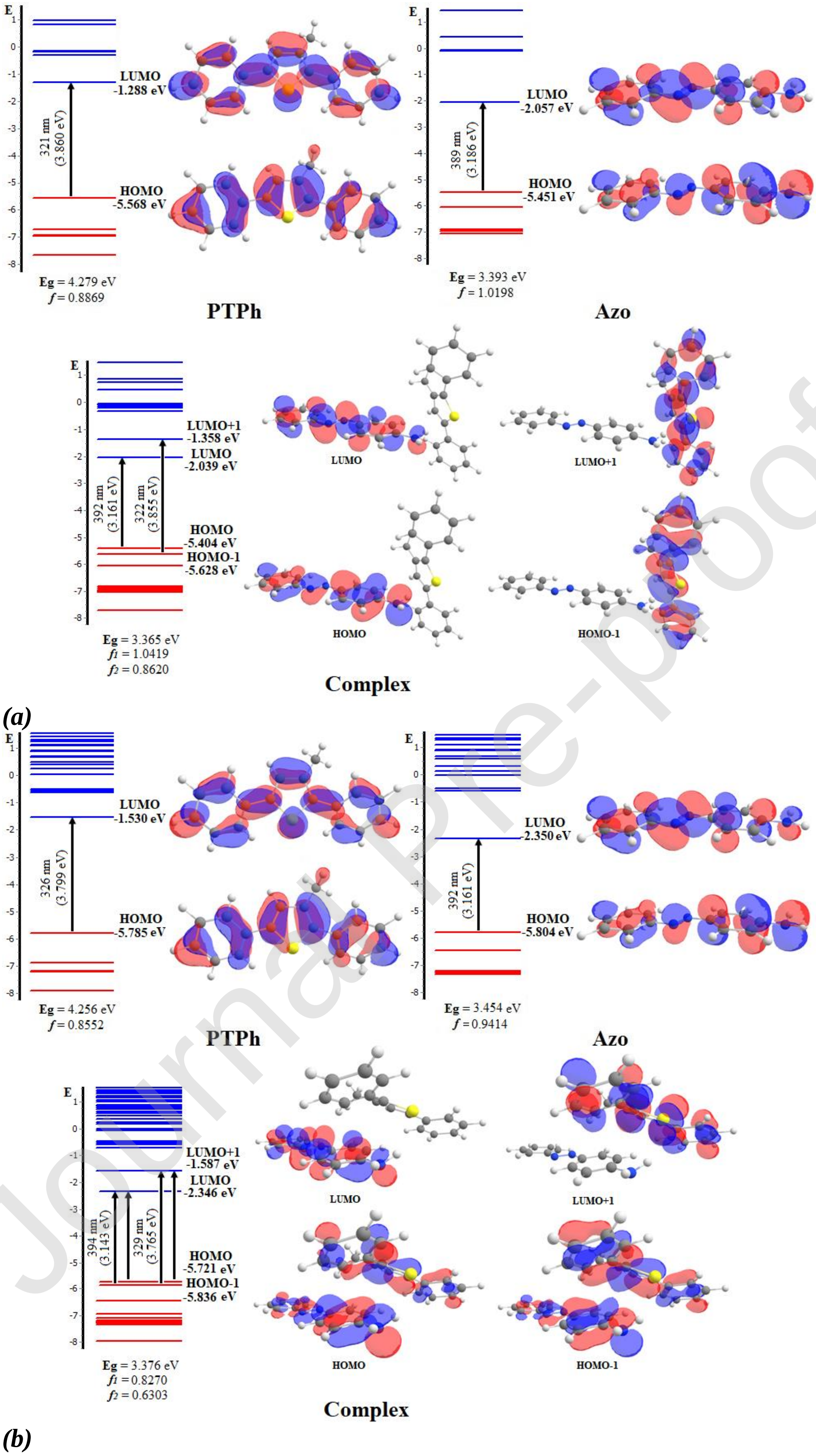


Figure 5 - Diagram energy and respective molecular orbitals of PTPh model, Azo and Complex for: ***(a)*** Complex 4; ***(b)*** Complex 8.

Conclusions

The composites formed by PTPh and Azo in solution results in systems of photophysics process of energy transfer were responsible for the efficiency of these materials. The suppression of PTPh luminescence by Azo indicated the energy transfer occurs from PTPh to Azo, and the process has greatest efficiency when ethanol was used as a solvent. To better understand the interactions in the system computational calculations were performed, indicating that NH---S and also C-H---π interaction might be involved in the energy transfer process of PTPh/Azo. Therefore, the joint computational-experimental study enabled to understand the energy transfer in the PTPh/Azo systems. These results show the viability of the system for the future application in a dosimeter.

CRediT author statement

Alessandra S. Menandro: Writing - Original Draft**. Leonardo J. A. Siqueira**: Software. **Hueder P. M. Oliveira**: Methodology. **Laura O. Péres**: Supervision, Funding acquisition, Writing - Review & Editing.

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