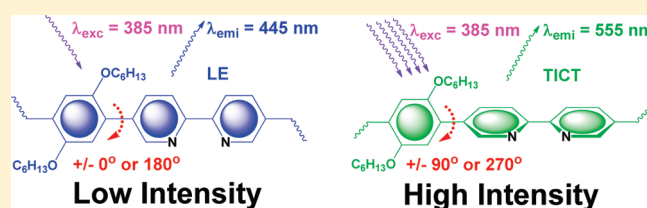


Optical Tuning of the Fluorescence Spectrum of a π -Conjugated Polymer through Excitation Power

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ABSTRACT: The photophysical properties of a π -conjugated polymer containing 2,2'-bipyridyl alternated with 2,5-dihexyloxyphenylene units (PBPyDHP) are investigated experimentally in terms of the conditions used (solvent, concentration, presence or absence of molecular oxygen, and optical excitation power). The experimental results have suggested that the fluorescence from PBPyDHP can be tuned by proper selection of the experimental conditions showing only one or two emission peaks: 445 nm (blue) and 555 nm (green). The observed effects were interpreted in terms of the twisted intramolecular charge transfer (TICT) theory. This is the first experimental report showing the interconversion of an usual fluorescence, called locally emission state (LE), to a TICT state in second scale time by varying the excitation power; that is, even though the torsion of only one fluorophore occurs in a nano or picosecond scale, the global change (the interconversion for all fluorophores) has occurred in the second time scale.



INTRODUCTION

In the last decades, we have seen the discovery of semiconductor properties of π -conjugated polymers, which have attracted increasing attention for their scientific interest and as potential materials for a wide range of device applications that combine the optoelectronic properties of semiconductors with the mechanical properties and processing advantages of plastics.¹

The application of conjugated polymers is advantageous when compared to conventional semiconductors in many applications, notably in OLEDs¹ and in photovoltaic cells.² The photophysical properties of such materials are not yet completely understood, specifically to the difficulty of correlating the polymer structure/morphology with optical properties. The main issue related to the emission properties of conjugated polymers is the assignment of its emissive centers. Apart from the intrinsic chemical composition and macromolecular architecture, the emission wavelength depends on two main parameters: the torsion angle of the conjugated backbone, which determines the effective conjugation length,³ and the occurrence of interchain interactions, leading to the formation of associated species, such as excimers and ground-state aggregates, and/or polaron pairs.⁴

Twisted intramolecular charge transfer (TICT) theory, introduced by Grabowski and co-workers,⁵ proved to be an excellent probe to study polymer segmental mobility. In TICT molecules, an electron donor (as an amino group attached to a π -system) and an electron acceptor unit (a nitrile group, for instance) are coupled through a pattern of alternating single and double bonds, and the two units can rotate relative to each other. After photon

absorption, already in the excited state, this rotation or twisting motion alters the fluorescence characteristics.^{5,6}

Photophysical properties of organic molecules are affected by the environment (e.g., solvatochromism⁷) and by the microenvironment. Particularly, the solvatochromism for small molecules is stronger than for polymers with the analogous structure, because apart from the solvent molecules the polymer units are surrounded by the polymer coil.⁸ The effect of the solvent on the polymeric morphology has also been investigated.^{4a,9} For fluorescence, it has been demonstrated that intensity is seriously affected by fluctuations in experimental conditions, as for instance the excitation power, solvent, and concentration.^{4b,7,9,10} Thus, by controlling the effects of such parameters, it is possible to access the influence of local structure on the photophysical properties.

It is well-known that polymeric structures containing groups like heterogeneous aromatic rings (e.g., pyridine, 2,2'-bipyridine, and 1,10-phenanthroline) have good thermal and oxidative stability, as well as interesting optoelectronic properties,^{1a,4b,8,10–12} apart from the possibility of metal (transition and lanthanides) complex preparation,^{1a,d,e,2a,8a} etc., making them very attractive for studying new properties and envisaging new opportunities. In this contribution, we report the study of the photophysical properties of a π -conjugated polymer containing 2,2'-bipyridyl

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groups alternated with 2,5-dihexyloxyphenylene units: poly[2,2'-bipyridyl-5,5'-diyl-(2,5-dihexyloxy-1,4-phenyl)] (PBPyDHP).¹¹ The dependence of the photophysical properties on the solvent polarity, molar concentration, and oxygen presence is demonstrated, as well as an unexpected dependence of the fluorescence peak on the excitation power, the emission mechanism of which is discussed in terms of TICT theory.⁵

EXPERIMENTAL SECTION

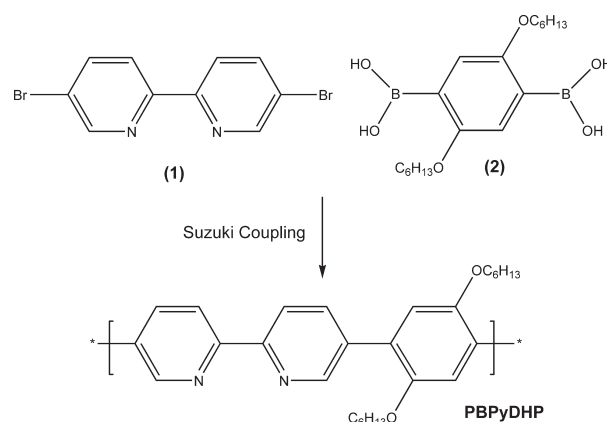
General. All syntheses were carried out under nitrogen atmosphere. The NMR analyses (¹H and ¹³C) were performed with a Bruker AC400 spectrometer, using CDCl₃ as solvent and TMS as internal standard. The infrared spectra (IR) were acquired in a Bruker IFS 66/s spectrometer using tablets of KBr. The molar masses of polymers were determined in a gel permeation chromatograph (GPC) model Waters WISP710B, running in tetrahydrofuran (THF), connected to columns SDV, with UV (S-3702; IT ADDS) and refractive index (LAUGHS, ERC 7512; WILD) detectors, and calibrated with polystyrene standards. The thermogravimetric analyses were carried out in nitrogen atmosphere at a heating rate of 10 K min⁻¹ using TGA/SDTA-851 (Mettler-Toledo).

Photophysical Analyses. The degassed solutions were prepared and sealed in an argon-filled glovebox with deaerated toluene and/or CHCl₃ as solvent. The quantum yield analyses were made by using CHCl₃ and toluene solutions (10⁻⁴ M) previously degassed in an argon-filled glovebox, using perylene as standard in toluene solution (10⁻⁶ M) previously degassed in an argon-filled glovebox (for more details, see the Supporting Information). The absorption spectra, all in solution, were recorded in a Shimadzu spectrometer model UV 2401 PC. Fluorescence measurements were done in a HORIBA JOBIN YVON Spectrofluorometer FluoroMax-4.

Ultrafast time-resolved fluorescence spectroscopy was performed using a Hamamatsu C4742 Streak Camera system working in synchroscan mode. The samples were excited using a frequency-doubled mode-locked Ti:Sapphire laser system operating at a repetition rate of 80 MHz (Mira 900 Optima, pumped with Verdi V5, both from Coherent Inc.). The pulse duration was approximately 200 fs. The excitation wavelength varied from $\lambda = 380$ nm to $\lambda = 430$ nm. By using the appropriate long pass edge filter (LP02-442RU-25, Semrock Inc.) or notch filter designed for $\lambda = 405$ nm (NF03-405 $\times 10^{-25}$, Semrock Inc.), the excitation wavelength was suppressed by more than 4 orders of magnitude. Special attention was dedicated to the spatial overlapping of the excitation and observation spot, and permanent control of the beam parameters was carried out. The laser beam had a diameter of approximately 1 mm. The sample fluorescence was collected by achromatic lenses (numerical aperture NA = 0.8) and dispersed by a 0.25 m monochromator with a 150 lines/mm grating before detection with the Streak Camera.

As excitation source for continuous wave (cw) luminescence measurements, a Nd:YAG (yttrium aluminum garnet) laser, stabilized in the ambient temperature, operating at $\lambda = 385$ and 405 nm was used. The luminescence spectra were registered by an Optical Multichannel Analyzer (OMA PMA-50 Hamamatsu Photonics Inc.). The measurements were done in time span of 60 s, and each 100 ms a single luminescence spectrum was recorded. Therefore, for measurement sequence, approximately 600 spectra were collected.

Scheme 1. Synthetic Route for the Preparation of the PBPyDHP^a



^a Conditions: Pd₂(dba)₃/DPEphos, 1–2.0 mol %, toluene, K₂CO₃ (aqueous solution 1 M), 90 °C, 72 h.

General Procedure for Preparing PBPyDHP. 5,5'-Dibromo-2,2'-bipyridine (0.300 g, 0.955 mmol), tris(dibenzylideneacetone) dipalladium(0) (0.0219 g, 24 μ mol), and (oxidi-2,1-phenylene)bis(diphenylphosphine) (0.0209 g, 38 μ mol) were added to 40 mL of toluene, under argon atmosphere and at room temperature (~ 20 °C). A degassed aqueous K₂CO₃ solution (12 mL, 1.0 M) was added to the mixture. After that, an ethanolic solution of 1,4-bis(boronic acid)-2,5-dihexyloxybenzene (11 mL, 0.367 g, 1.003 mmol) was added to the mixture toluene/water. The solution was degassed, heated to 95 °C, and kept under vigorous stirring and argon atmosphere for 72 h. After being cooled to room temperature, the mixture was poured on stirred methanol. The precipitate was collected by filtration. Filtration and drying under vacuum yielded 180 mg (44%) of PBPyDHP as a yellow powder. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.92 (d, 2H), 8.45 (2d, 2H), 8.11 (2d, 2H), 7.10 (s, 2H), 4.00 (t, 4H), 1.75 (m, 4H), 1.25 (m, 12H), 0.87 (t, 6H). ¹³C NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 13.0, 21.5, 24.7, 28.3, 30.4, 68.7, 114.5, 119.3, 126.9, 132.9, 136.7, 148.6, 149.7, 153.5. FTIR (KBr pellets, cm⁻¹): 3046, 2968, 2925, 2849, 1596, 1517, 1265, 1089.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. PBPyDHP was prepared following published procedures¹¹ (the structure and the conditions are shown in Scheme 1). The molar mass determined by GPC was MW = 5585 g mol⁻¹ and polydispersity of 2.87, indicating that the degree of polymerization was about 12–13. Considering published results that have demonstrated that the effective conjugation length does not surpass two repetitive units,¹² the MW was valid for photophysical measurements. The polymer structure was confirmed by FTIR and by ¹H and ¹³C NMR spectroscopies, and showed good solubility in CHCl₃ and toluene and moderate solubility in dichloromethane and THF, with good thermal stability (higher than 350 °C for 10% weight loss).

Photophysical Characterization. Toluene and CHCl₃ solutions, with different concentrations (from 10⁻⁵ to 10⁻³ M), were analyzed by ultraviolet–visible absorption spectroscopy (UV–vis). No relevant changes in the absorption spectra were observed, even with the wide range of concentration used and the

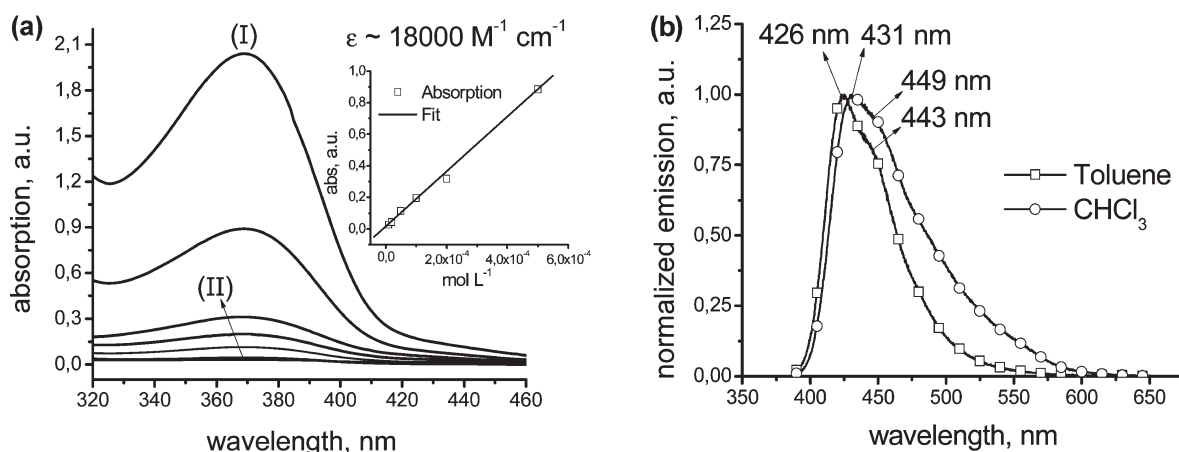


Figure 1. (a) UV–vis absorption spectra of CHCl_3 solutions. (I) stands for 1×10^{-3} M and (II) for 1×10^{-5} M. Inset shows the linear fit for the determination of the molar extinction coefficient (ϵ). (b) Normalized emission spectra of toluene and CHCl_3 solutions ($\lambda_{\text{exc}} = 370$ nm, 1×10^{-5} M).

Table 1. Decay Time Data (in picoseconds, ps) for Degassed and Nondegassed CHCl_3 and Toluene Solutions

conc. (M)	toluene (with O_2)	toluene (no O_2)	CHCl_3 (with O_2)	CHCl_3 (no O_2)
10^{-3}	825 ^a	910 ^a	980 ^b	910 ^b
10^{-4}	810 ^a	885 ^a	850 ^b	697 ^b
10^{-5}	852 ^a	645 ^a	660 ^b	580 ^b

^a Peak at 437 nm. ^b Peak at 445 nm. ^c Peak at 540 nm. ^d No peak was observed at 540 nm for degassed CHCl_3 solutions 10^{-3} M.

difference between polarities of the solvents. It is an indication that, in such conditions, the ground state was not affected: no aggregated species were formed, and no solvatochromic effect took place. A maximum absorption peak at 370 nm ($\pi \rightarrow \pi^*$ transition) was observed for both solvents and all concentrations, with absorption edge around 420 nm. Figure 1a shows the UV–vis spectra of the degassed CHCl_3 solutions. The molar extinction coefficient (ϵ) was calculated using the Beer–Lambert law, giving $\epsilon \approx 18\,000 \text{ M}^{-1} \text{ cm}^{-1}$, for both solvents with and without oxygen. The fluorescence emission spectra were collected by a conventional spectrofluorometer. The main emission peaks were at 426 nm for toluene and at 431 nm for CHCl_3 (Figure 1b, $\lambda_{\text{exc}} = 370$ nm). The emission peaks did not shift when the excitation wavelength was changed from 385 to 405 nm. The spectra showed a shoulder at 443 nm and one at 449 nm, for toluene and CHCl_3 , respectively.

The determination of the excited-state decay times (τ) of PBPYDHP was performed in CHCl_3 and toluene solutions, with and without oxygen, for concentrations from 10^{-5} to 10^{-3} M. The data for toluene solutions presented in Table 1 have not shown important changes, with decay times somewhat longer for degassed than for nondegassed solutions. One value, however, was shorter than the expected with $\tau = 645$ ps (10^{-5} M, without O_2), which will be discussed further on. The time-resolved emission spectra presented only one emission peak at 437 nm (red-shifted in comparison with the spectra collected by the spectrofluorimeter). On the other hand, significant changes were detected for the CHCl_3 solutions. For the nondegassed ones, the time-resolved emission spectra were red-shifted in comparison with the spectra collected by the spectrofluorimeter as well (from 431 to 445 nm). The more diluted solution (10^{-5} M) showed a shoulder at approximately 540 nm (Figure 2a), and the decay time for such solution is shorter than that observed for toluene at

the same conditions (see Table 1), indicating that the excited state in CHCl_3 is less stable than that in toluene.

Regarding the degassed solutions (Figure 2b), it was observed that the emission location and decay times depended on the concentration. For concentrated solutions (10^{-3} M), only one emission peak (at 445 nm) was observed. For the diluted ones (10^{-5} M), the emission peak shifted to 540 nm, while for 10^{-4} M two emission peaks were observed (at 445 and 540 nm). The emission peak at 445 nm had a shorter decay time than that measured in nondegassed solutions (for all concentrations), whereas that at 540 nm had a longer, indicating a higher stability of the species emitting at 540 nm (Figure 2c and d).

The above results were not expected, because the classical behavior would be a red shift only for concentrated solutions and not for the diluted ones, as described in the literature.¹³ It was also noticed that the dual emission takes place only when PBPYDHP solution was irradiated with higher excitation power provided by the Ti:Sapphire laser system, indicating the existence of an unexpected dependence on the emission upon the excitation intensity. When a standard spectrofluorometer (lower excitation intensity) was used, the effect was not observed, under identical experimental conditions.

The reason for the dual emission and the different decay times of PBPYDHP was interpreted in terms of conformational changes in the excited state, because no changes were observed in the absorption spectra. Molecules containing both donor (e.g., alkoxy phenylenes) and acceptor (e.g., 2,2'-bipyridyl) electron groups can undergo photophysical intramolecular processes involving electron transfer between those centers, that is, a photoinduced intramolecular charge transfer (ICT).⁵ ICT might induce conformational changes in the molecule like a rotation of the chemical bond between acceptor and donor electron groups, giving rise to two emission peaks (dual emission), which would be detected under specific experimental conditions.

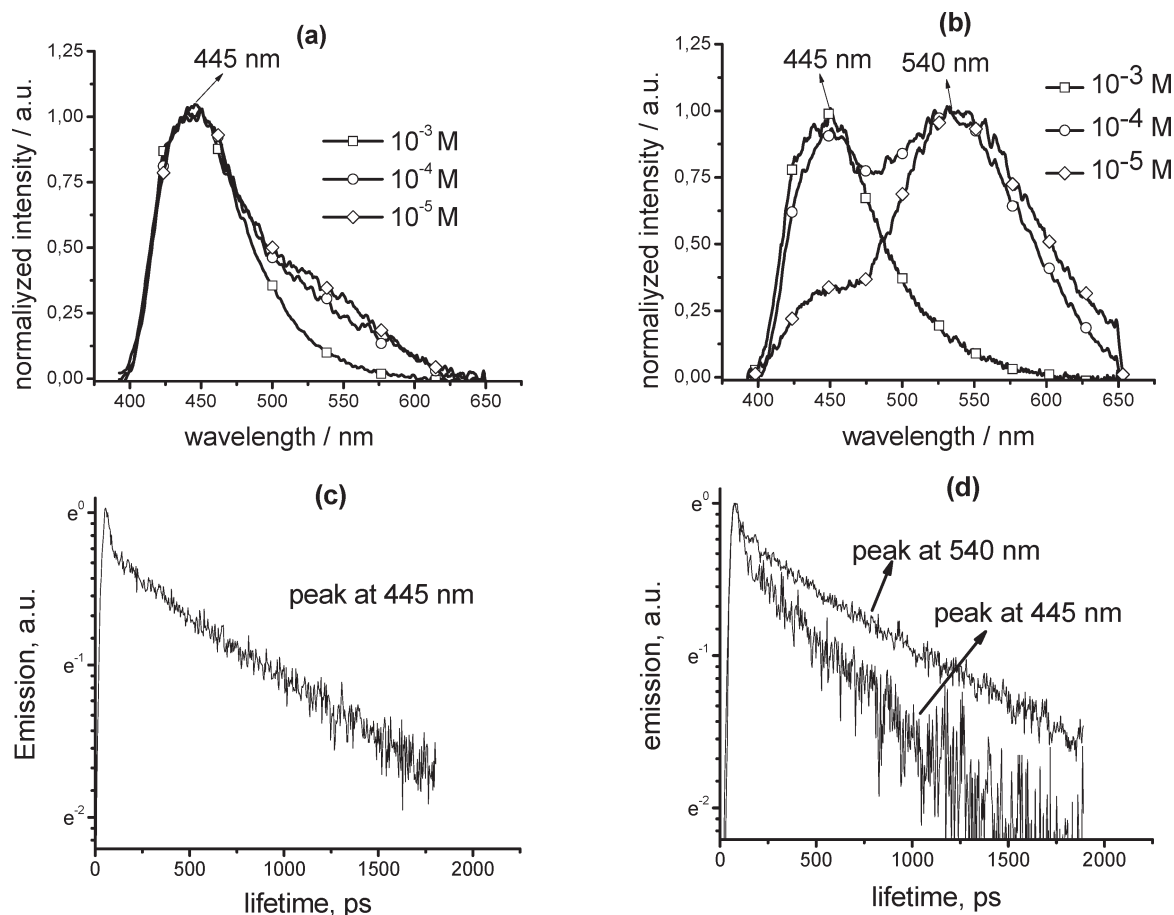


Figure 2. Emission spectra collected in the Streak Camera for nondegassed (a) and degassed (b) CHCl_3 solutions in different concentrations (10^{-3} , 10^{-4} , and 10^{-5} M); decay time curves for nondegassed (c) and degassed (d) CHCl_3 solutions (10^{-5} M).

The dual emission of the 4-dimethylamino benzonitrile (DMABN) molecule has been known since 1961, when Lippert's work was reported.¹⁴ Since then, some theories have been proposed to explain the emission mechanism.^{5c,e,7} One of these theories is the twisted intramolecular charge transfer (TICT) theory. The TICT theory states that the original excited state (which is planar and called locally excited state, LE) is responsible for the usual fluorescence, while a second excited state (resulting from twisting of the donor moiety to a perpendicular geometry relative to the rest of the molecule) presents a red-shifted emission, called the TICT excited state.⁵ The results presented here support such theory. In the present case, the electron donor group is the alkoxy phenylene unit, and the acceptor is the bipyridylene unit. A schematic illustration of the energy barriers related to the TICT and LE states is depicted in Figure 3.

The occurrence of TICT requires specific conditions, and among the main factors affecting the process there are solvent polarity, viscosity, temperature, and concentration, apart from the proper chain conformation.^{5,7} These factors will be discussed further on for the present case. Apart from the ICT theory, other interpretations for the observed dual emission could be considered:

- (1) Formation of aggregated species: That hypothesis was ruled out because the phenomenon was observed only in diluted solutions. Later, it will be shown that as the concentration increases, the observation of such phenomenon becomes more difficult. It seems that intermolecular

interactions hinder the interchange between the two conformations, strengthening the idea of an intramolecular effect.

- (2) A conformation with higher planarity would be assumed by the chains in the excited state, increasing the effective conjugation length, giving rise to a red-shifted emission: This is not applicable for our system. It was demonstrated that, for polymers containing 2,2'-bipyridine units, the effective conjugation length is not larger than two repetitive units.¹² The fluorescence emission centered at 445 nm corresponds to this conjugation length.
- (3) Higher excitation power can modify the ratio between emitting centers in the excited state and those in ground state. Such an optically excited system could bring about changes in the emission spectra and/or quantum yield: This, however, neither explains why the effect occurs only for specific solvent (CHCl_3) but not for toluene, nor explains the variation of the decay time of the excited state. Earlier, it was shown that the decay time of the excited state does not depend on the excitation power.¹⁵
- (4) E-type delayed fluorescence is observed when the energy difference between singlet and triplet states is small and when the decay time of triplet is long enough. The resulting fluorescence emission has the same spectral distribution as the prompt fluorescence but with longer decay time, at the scale of microseconds.¹³ This interpretation cannot be considered, because the spectral

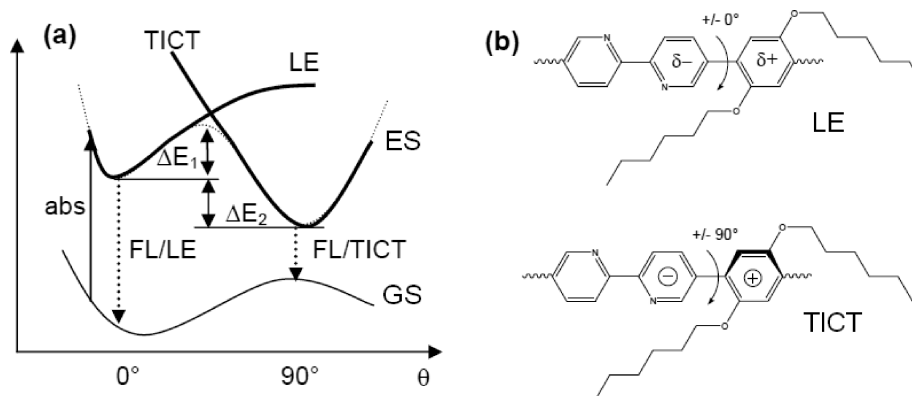


Figure 3. Schematic illustration of the energy barriers related to the TICT and LE states in PBPyDHP. ES and GS stand for the excited and ground states, respectively; abs for absorption; ΔE_1 is the difference of energy between LE and TICT states, and the ΔE_2 is the barrier to be overcome to attain TICT (a). Representation of the LE and TICT conformers (b).

distribution of the emission is changed, and the decay times are not significantly influenced, for both peaks.

- (5) Phosphorescence is observed at longer wavelengths, and the decay times are longer in comparison with the fluorescence lifetime.¹³ This assumption is not applicable because the decay times for both peaks are comparable, on the order of 1 ns.

The results led us to suggest that higher excitation power could lead to the absorption of more than one photon per polymer molecule, considerably altering the excited state and saturating the fluorescence at 445 nm. That would give rise to the formation of a new twisted state, stable only in higher polarity media. In other words, depending on the excitation power, two excited states would be formed (the LE and/or the TICT), and the emission would be located in the blue or/and in the green region of the spectrum. The stability of these forms is a function of the experimental conditions.

Considering the results observed with toluene, the decay times show that only LE emission takes place with this solvent. However, for degassed diluted solutions, the decay time is short enough ($\tau = 645$ ps, see Table 1) to indicate an incipient formation of the TICT state. In CHCl_3 , it is already possible to observe such tendency in diluted and nondegassed solutions, due to its higher polarity in comparison with toluene, which explains the absence of the peak at 540 nm for toluene. These results agree with literature data⁵ and led us to suggest that there is a small energy barrier between the two states, which is affected by the polymer chain conformation.

Previous experimental works indicated that the fluorescence in polymers does not depend only on the solvent polarity³ (which controls the occurrence of interchain interactions, leading to the formation of excimers, aggregates, and/or polaron pairs) but on the torsion angle of the conjugated backbone as well, which determines the conjugation length.⁴ For small organic molecules, solvent polarity and viscosity play a crucial role in the formation of the TICT, but for large molecules such as polymers or oligomers, other requirements must also be met. In small molecules, bulky substituents can hinder the molecular twisting.⁵ The torsional motion around the carbon–carbon single bond in the 2,2'-bipyridine, for instance, is possible at room temperature. The cisoid and transoid forms are in equilibrium, and the rotational barrier of such motion is of approximately 31 kJ mol⁻¹.^{14,16} Klosterman et al. presented their results concerning

a series of manisyl-substituted pyridyl-phenanthrolines, which are similar to the repeating unit of PBPyDHP.^{5h} Whereas in the former case the donor and acceptor were held orthogonal, that is, pretwisted systems,^{5c,i,j} here the donor and the acceptor are “free” to rotate. However, in polymers, many types of relaxations, short and long, are present,^{17,5i} which preclude the necessary rotation to achieve the geometry for the TICT state, resulting in a higher energy input to attain that state.

In the scheme of Figure 3, the energy levels involved in the transitions are presented, where ΔE_1 is the difference in energy between LE and TICT states and the ΔE_2 is the barrier to reach TICT, which occurs only after LE saturation and the proper conformation is attained. The scheme also illustrates why there are different emission wavelengths, because each excited state is related to a different conformation with specific stabilization energy.

An experiment was performed in which the excitation power was varied and the fluorescence was monitored, keeping all other conditions constant (excitation wavelength, concentration, temperature, and presence of oxygen).

A laser system was used as excitation source, applying wavelengths of 385 and 405 nm for degassed CHCl_3 diluted solutions. The analysis of the experimental data shows that an increase of the excitation power leads to a marked distortion of the profile of the fluorescence band: at the beginning of the experiment, when the light reaches the sample and the first data are collected, emission at 445 nm appears. Immediately afterward, a peak at 555 nm starts to grow up. It is important to notice that the effect is reversible: if the light is switched off and on again, the same change is observed, either with excitation of 385 or 405 nm. Emission shifting with time has already been published, demonstrating the effects of polarity and temperature on the formation of the LE and TICT states of specific molecules.¹⁸ However, in the reported case, the interconversion between the LE and TICT states underwent in a nanosecond regime, and in the present situation we observed that the global process can take a few seconds, depending on the excitation power, as demonstrated below.

After the measurements, the solutions were analyzed by means of UV–vis spectroscopy. The observed absorption and emission spectra coincided perfectly with the former spectra, observed before the optical pumping process. One can conclude that no photochemical reactions had occurred during the irradiation. This is important information, because it discards the hypothesis

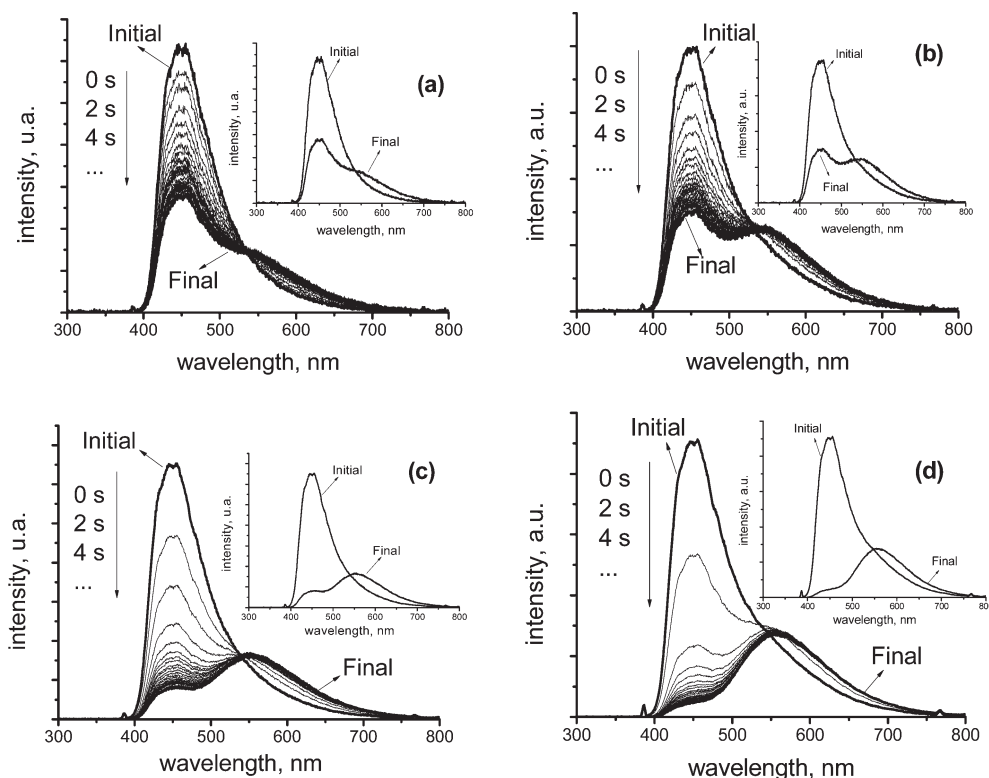


Figure 4. Variation of the luminescence profile with time using different excitation power: (a) $10\ \mu\text{W}$, (b) $20\ \mu\text{W}$, (c) $50\ \mu\text{W}$, and (d) $100\ \mu\text{W}$. Samples were degassed; CHCl_3 solutions $10^{-5}\ \text{M}$; $\lambda_{\text{exc}} = 385\ \text{nm}$. Each spectrum was taken at every 2 s (see the movie file available in the Supporting Information).

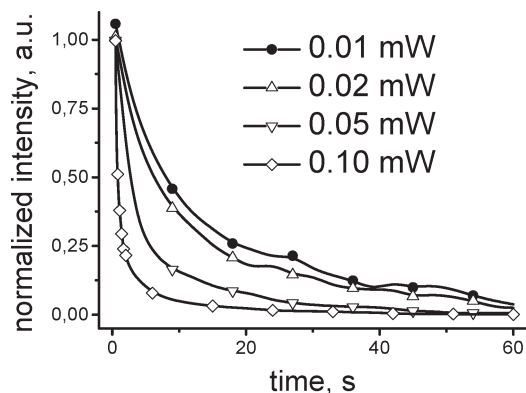


Figure 5. Dependence of the temporal dynamics of fluorescence spectra showing the decrease of the emission intensity of the blue region (centered at $\lambda = 445\ \text{nm}$) in 60 s for different excitation power, CHCl_3 , $10^{-5}\ \text{M}$.

of a reaction between the solvent and the polymer, which would bring about chemical changes in the sample, modifying its optical properties.

When the excitation power was varied from $10\ \mu\text{W}$ to $5\ \text{mW}$, it was observed that the kinetics of the process depended on the intensity of the incident radiation, being faster for higher excitation power. Figure 4 displays the luminescence spectra for degassed CHCl_3 solutions ($10^{-5}\ \text{M}$, $\lambda_{\text{exc}} = 385\ \text{nm}$) with excitations power from $10\ \mu\text{W}$ (a), $20\ \mu\text{W}$ (b), $50\ \mu\text{W}$ (c), and $100\ \mu\text{W}$ (d).

Table 2. Solutions of Toluene/ CHCl_3 (N_n Is the Solution's Number, from 1 to 8)

CHCl_3	toluene, v/v % ($10^{-5}\ \text{M}$)
$N_1 - 1 \times 10^{-5}\ \text{M}$	$N_5 - 0\% \text{CHCl}_3$
$N_2 - 2 \times 10^{-5}\ \text{M}$	$N_6 - 10\% \text{CHCl}_3$
$N_3 - 5 \times 10^{-5}\ \text{M}$	$N_7 - 20\% \text{CHCl}_3$
$N_4 - 10 \times 10^{-5}\ \text{M}$	$N_8 - 50\% \text{CHCl}_3$

The results clearly show that increases in the excitation power accelerate the process. The expected red shift, typical for a TICT emission, is also clearly observed. The emission shifting with time is followed by a decrease in the excited-state energy level, because the difference between the maximum emission peaks is $4454\ \text{cm}^{-1}$ (445 moves to $555\ \text{nm}$, or $22\,472$ to $18\,018\ \text{cm}^{-1}$), which corresponds to $12.74\ \text{kcal mol}^{-1}$ (see ΔE_1 in Figure 3). It is noteworthy that the emission intensity decreases in TICT, as compared to LE emission, which means that TICT has smaller quantum yield (QY) than LE. This parameter was calculated using perylene as standard (see the Supporting Information). For measurements in spectrofluorometer, the LE QY is in the 60% range (58% for toluene and 61% for chloroform) with excitation at $370\ \text{nm}$, whereas at $405\ \text{nm}$ the QY dropped down to the 40% range (35% for toluene and 41% for chloroform). No TICT emission was observed when the PBPdHP was analyzed by spectrofluorometer. Under laser excitation, the chloroform solution showed both LE and TICT fluorescence (depending on the excitation power), and the QY dropped down from 35% to around 12% (LE and TICT emission, respectively; excitation

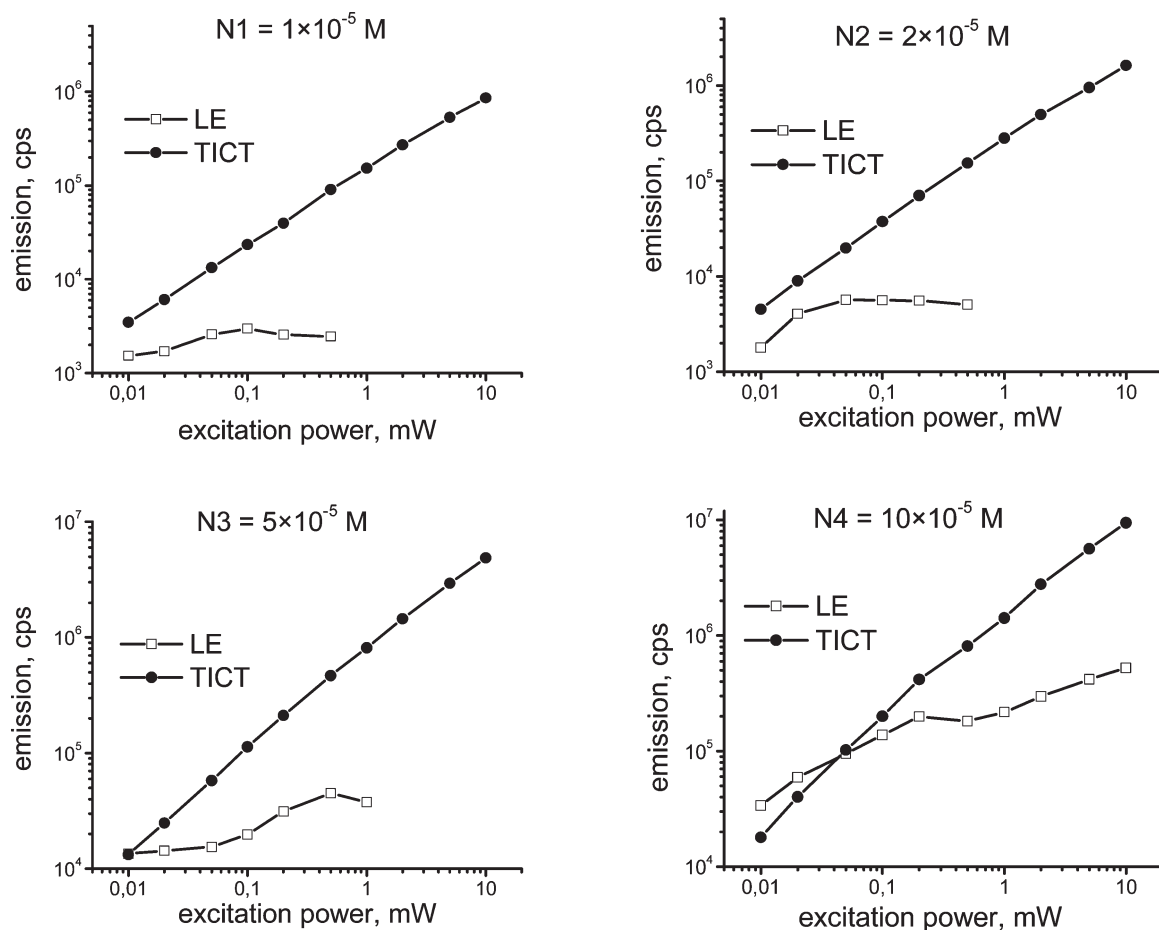


Figure 6. Variation of the LE and TICT emissions with concentration and excitation power (see Table 2), $\lambda_{\text{exc}} = 385$ nm.

wavelength $\lambda = 405$ nm), whereas in toluene the QY dropped down from 35% to around 16%. One of the features of TICT processes is that with increasing polarity, the fluorescence quantum yield decreases.⁵ In our case, the QY for toluene (LE emission) is higher than that in chloroform (TICT emission) at higher excitation power.

Molecular switches have so far been synthesized on the basis of systems whose emission properties can be modulated by external inputs, such as pH,^{19a,b} light,^{19c,d} and metal ion exchange.^{19e} PBPyDHP can be a new molecular light intensity-dependent optical switch. As the excitation power is increased, PBPyDHP switches the emission from 445 to 555 nm.^{15b}

The dependence of the response time on excitation power, where the LE fluorescence (centered at $\lambda = 445$ nm) of PBPyDHP decreases, is shown in Figure 5. The experimental parameters such as local temperature, polymer concentration, and solvent were kept constant. The optical density of the sample is rather small ($\text{OD} = 0.08$). The switching time decreases significantly when the excitation power increases: from almost 60 s at 20 μW , down to less than 1.0 s at 100 μW (measured at 1/e level; more results in Figure 9).

The shift of the emission peak is mainly affected by concentration, polarity of the solvent, the presence of O_2 , and the excitation power. These are discussed in detail further on. To understand the effect of the concentration and the polarity, solutions with different concentrations and polarities have been prepared, using toluene and CHCl_3 , which are the best solvents

for this polymer, preventing undesirable effects as precipitation or aggregate formation, which could mask the results. All of the solutions were degassed. A summary of the prepared solutions is shown in Table 2.

Effect of Concentration. Degassed solutions with concentrations between 1×10^{-5} and 10×10^{-5} M were prepared, all in CHCl_3 . The LE emission was observed in more concentrated solutions, whereas in diluted ones the TICT emission predominated. Figure 6 shows the dependence of the fluorescence emission behavior of the polymer on the concentration. LE emission increased when the concentration was increased.

For concentrations of 1×10^{-5} , 2×10^{-5} , and 5×10^{-5} M, no LE emission was detected when the excitation power was above 500 μW (N_1), 500 μW (N_2), and 1 mW (N_3), respectively (see Figure 6). The free-volume effect plays a major role in the TICT processes in polymer environment, because there will be more free volume for the twisting to occur in more diluted conditions than in concentrated ones.^{5e,15a,17,20} It is also possible to assume that the increase of the number of collisions of the polymer with the neighborhood in higher concentrations will contribute to deactivate the TICT species. Because of the sensitivity of the TICT emission to polymer environment, such system can be utilized as a probe to study the mobility of polymer segments.²⁰

Effect of Polarity. The influence of the polarity of the medium was studied by varying the ratio of CHCl_3 /toluene mixtures used as solvent, going from zero (pure toluene) to 0.5. Chloroform is

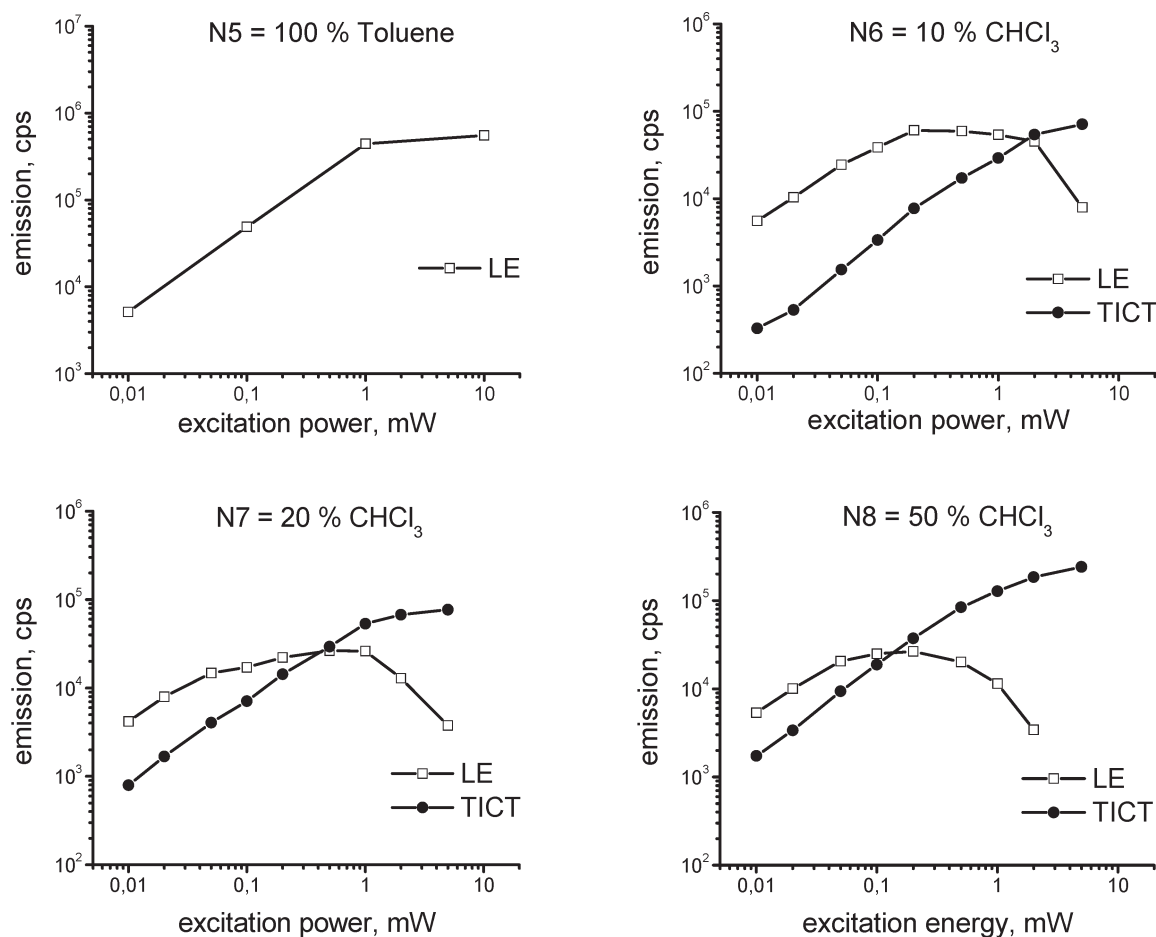


Figure 7. Variation of the LE and TICT emissions with solvent polarity (see Table 2), $\lambda_{\text{exc}} = 385$ nm.

more polar than toluene (dipolar moments = 1.15 and 0.36 D, respectively). These results are shown in Figure 7.

Because the increase in polarity increases the rates of formation of the TICT state, it was assumed that the solvation of the polymer chains in twisted conformation is better in CHCl_3 than in toluene.^{5c} Thus, the higher is the percentage of CHCl_3 , the easier is the stabilization of an excited state with higher polarity (TICT state), and the possibility of the TICT formation increases as well. The solvation power of a solvent depends on mainly on its polarity. In a polymeric system, solvents as THF and CHCl_3 solvate preferentially the lateral groups, while others as chlorobenzene or toluene solvate the main chain.^{4a,7,9a}

Thus, depending on the type of solvent, different macromolecular conformations might exist and, therefore, different effective wavelengths and different profiles of fluorescence.^{4a,9a} Another finding was that increases in polarity resulted in decreases in excitation power needed for both of emissions had equal intensities; that is, the greater is the polarity, the easier is for TICT emission intensity to overcome the LE emission. For instance, for the solution containing 10% CHCl_3 , the power needed was 2 mW, and for pure CHCl_3 it was less than 10 μW , or 2 orders of magnitude less (see Figure 7 and N_1 in Figure 6).

Effect of Oxygen. The deactivating effect of oxygen on TICT has been linked to the formation of triplet species in high yield for oligomers and polymers,^{5d} affording an explanation for the fact that in the presence of oxygen the TICT state is easily deactivated. This phenomenon is easily shown in Figure 2. In normal

conditions, the polymer solutions containing oxygen showed shoulders in the green region, indicating that TICT might occurred, but in low yield. The emission at 555 nm was more clearly observed with increases in excitation power. For example, solutions with concentrations of 10^{-4} M required an increase of 2 orders of magnitude in excitation power for the detection of the green emission.

When the solutions were degassed with argon, the less concentrated ones showed TICT emission even at low excitation power, and concentrated solutions showed the usual blue emission only. According to the literature, the twisted conformation in the excited state increases the spin–orbit coupling; thus TICT would bring about an increase in intersystem crossing (ISC) in relation to LE.^{5c,f} Moreover, an increase in polarity increases the formation of the TICT state (as noted in Figure 7) and also affects the rates of ISC.¹³ It is well-known that oxygen is a quencher of triplet species in organic compounds, and that would explain the difficulty in observing TICT emission in nondegassed solutions. In conclusion, one can say that in polymers, the TICT requires high energy to be formed, and, when that occurs, it is easily deactivated by ISC due the high rates of the triplet state formation, which is in agreement with the quantum yield results (see the Supporting Information).⁵ Therefore, to observe fluorescence from it, high energetic input is necessary for its formation and more again to keep it emitting luminescence. Luminescence-based optical sensors as O_2 quenching sensors are important in biological systems, and the high O_2 sensitivity of the PBPdHP might be useful for the development of such type of sensor.²¹

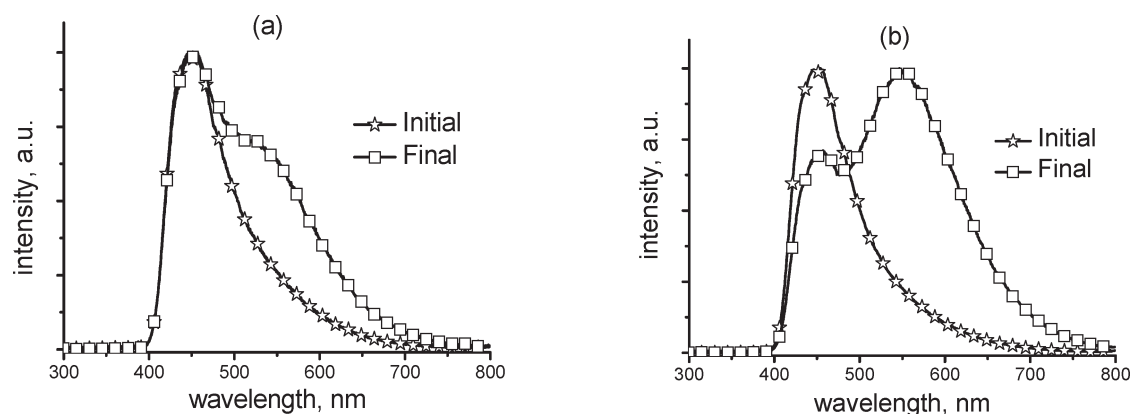


Figure 8. Effect of the presence of oxygen on the emission profile of PBPyDHP. Experimental conditions: 2 mW, 1×10^{-4} M, CHCl_3 , with O_2 (a); 100 μW , 1×10^{-4} M, CHCl_3 , without O_2 (b).

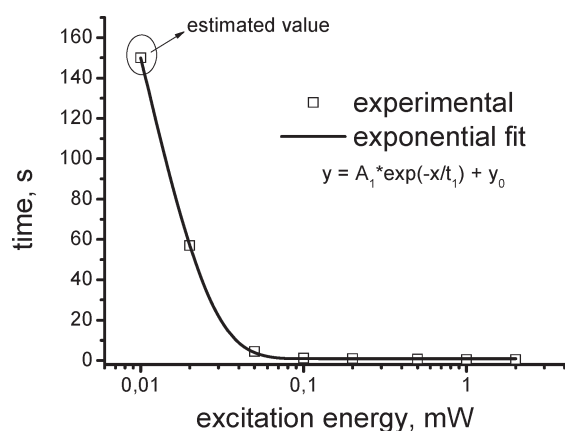


Figure 9. Variation of response time with excitation power. Each measurement corresponds to a decrease of $1/e$ of the LE emission (peak at 445 nm) intensity of PBPyDHP. Degassed CHCl_3 solutions, 1×10^{-5} M.

Figure 8 illustrates the magnitude of the effect brought about by the presence of oxygen. For nondegassed CHCl_3 solutions at 10^{-4} M (Figure 8a), the green emission needed 2 mW to be observed, whereas the degassed solution showed TICT emission with excitations as low as 100 μW (Figure 8b). For convenience, only the initial and the final spectra are shown.

It is noteworthy that an energy diagram was reported for the singlet (S) and triplet (T) energy levels of LE and TICT states regarding the DMABN molecule.^{5k} The diagram considers that the triplet energy level associated with TICT is higher than that for the LE state, which is in agreement with the results so far presented for PBPyDHP.

Effect of Excitation Power. In conventional spectrofluorimeter measurements, PBPyDHP solutions presented the usual blue emission around 420–450 nm. Figures 4 and 5 illustrate the importance of the excitation power as already discussed. To make the interpretation of the results easier, Figure 9 was constructed. As was pointed out previously, increases in the excitation power brought about a higher rate of change of LE to TICT emission. Taking the time needed for the LE emission decay of $1/e$ ($t^{1/e}$ or τ' ; it should not be confused with τ for decay time) in each measurement, it was observed that an exponential dependency exists between τ' and the excitation power, as shown in the graph.

This result is in agreement with the idea of the existence of an energy barrier between LE and TICT as illustrated in Figure 3.

In the present case, the barrier is related to the energy required to twist the fluorophore linked into the polymeric backbone after the saturation of the LE state and to keep such state emitting luminescence. In conventional spectrofluorimeters, the intensity of the incident beam is not enough to provide such saturation and then the torsion, and thus TICT cannot be observed.

We believe that the time scale in which the phenomenon was observed is due to the fact that the active center is linked along a polymer backbone, and thus subjected to the chain conformations. To our best knowledge, this is the first time that a molecular interconversion in the scale of seconds (in real time) has been detected. It is important to note that, whereas the twist of one fluorophore occurs in the scale of nano/picoseconds,¹⁸ the global change (interconversion from LE to TICT for all fluorophores) takes place in the scale of seconds for PBPyDHP. Other studies, regarding the effect of different solvents and the temperature on the polymer emission, have been done, and they will be published elsewhere.

CONCLUSIONS

The experimental results indicate that that emission of PBPyDHP occurs from two different excited states (due to different conformations, TICT and LE) with emission peaks at 430–450 and 540–555 nm regions of the electromagnetic spectrum. The first one is the usual emission, the LE state, and the second one can be observed only in certain conditions accompanied/ followed by structural changing of the molecule in the excited state, and was ascribed to the TICT state.

The segmental movements present in polymers can hinder the formation of the TICT state, even though its generation is possible. For small molecules, the twisted state is easier to be formed, and the charge separation as well. The vibrational movements are more defined and simpler, the number of degrees of freedom is larger, and lesser energy is required to stabilize the TICT excited state.

Because of the sensitivity of the TICT emission to polymer environment, this system can be utilized as probe to study the mobility of polymer segments. Its O_2 sensitivity might be applied in oxygen sensors, as well as new molecular switch, due its light intensity-dependency: with increasing excitation power, PBPyDHP switches its emission from 445 to 555 nm.

■ ASSOCIATED CONTENT

S Supporting Information. Data regarding the quantum yield measurements of the PBPYDHP; a video showing the emission shift from LE to TICT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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