

UV-Vis and fluorescence study of polyacetylenes with pendant 1-pyrenyl groups: a comparative investigation of *cis*- and *trans*-poly(1-ethynyl-pyrene)

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Abstract

The optical and photophysical properties of *trans*-poly(1-ethynyl-pyrene) (*trans*-PEP) and *cis*-poly(1-ethynyl-pyrene) (*cis*-PEP) are reported. From the absorption spectra of both polymers, it is found that *trans*-PEP possesses a higher degree of conjugation than its *cis* analogue. On the other hand, intramolecular interactions occur between the pendant pyrene units (associated pyrenes) present in each polymer, giving rise to a new emission. These interactions are stronger in the *cis*-PEP, probably due to coiling of the main polyacetylene chain. Excitation spectra combined with fluorescence decay profiles show that these interactions occur in the ground state (excited complex).

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1. Introduction

Substituted polyacetylenes, like many other conjugated polymers, are regarded as promising materials for the development of optoelectronic devices such as light emitting diodes, photovoltaic cells and non-linear optical systems [1–3]. The optoelectronic properties vary significantly depending on the configuration and the regularity of the main chain, the nature of the substituents, the degree of the extended conjugation, and the distortion of the main chain induced by the steric effects of the substituents [4].

The presence of substituents on polyacetylenes generally reduces conjugation, because of the twisting of the main chain caused by the repulsion of the pendant groups. The introduction of condensed aromatic rings, however, tends to give highly conjugated and well-defined polymers, with stacking of the pendant groups [5,6]. As a part of a continuing research effort in the development of new materials for molecular electronics [7,8], we prepared novel polyacetylenes with pendant pyrenyl groups bound directly to the

main chain. This new molecular architecture would serve as a model for the future synthesis of conducting polymers containing internal stacking of aromatic units and bearing some groups able to stabilize the formation of charge carriers.

Masuda and co-workers carried out the polymerization of 1-ethynyl-pyrene obtaining poly(1-ethynyl-pyrene) (PEP) with a *trans*-transoidal geometry and molecular weights M_w varying from 1.2×10^4 to 4.7×10^4 Da [9–11]. In a separate study, our research group optimized the reaction conditions for the polymerization of this monomer and obtained *trans*-PEP with much higher molecular weights M_w ranging from 2.4×10^4 to 40×10^4 Da and wide polydispersities from 2 to 10 [12]. The group of Masuda also prepared PEP bearing a *cis*-cisoidal geometry using $\text{Rh}_2\text{nbdc}_2\text{Cl}_2$ as a catalyst. The resulting polymer, however, is practically insoluble and difficult to characterize [11]. Our research group recently reported the optimized synthesis and characterization of a highly soluble poly(1-ethynyl-pyrene) bearing *cis*-transoidal configuration (*cis*-PEP) using a nickel complex, (1-Me-Ind)Ni(PPh₃)C≡CPh, as a catalyst and MAO as a co-catalyst [13].

In the present work, the optical and photophysical properties of the *cis*- and *trans*-PEP are reported emphasizing the nature of the electronic interactions involved among adjacent pendant pyrene groups linked to the polyacetylene

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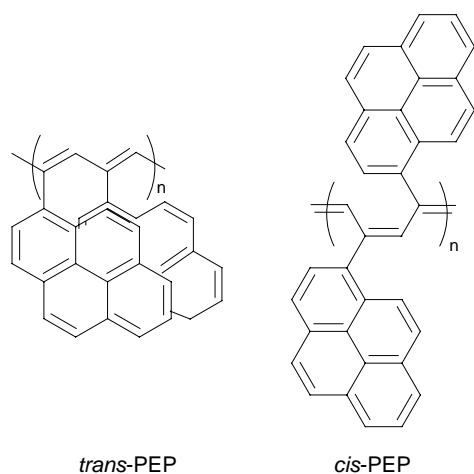


Fig. 1. Molecular structures of the polymers investigated.

chain. It is observed that the *cis*-PEP is less conjugated than the *trans*-PEP giving rise to stronger static molecular interactions between pyrenyl moieties by coiling of the main polyacetylene chain.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was purchased from Aldrich (spectrophotometric grade). Prior to use, the solvent was checked for spurious emission in the region of interest and found to be satisfactory. The synthesis of *trans*-poly(1-ethynyl-pyrene) (*trans*-PEP) [12] and *cis*-poly(1-ethynyl-pyrene) (*cis*-PEP) [13] was achieved according to our previously published

procedures. Polymers having similar molecular weights M_w (24 000 g/mol) have been used in this work.

The chemical structures of *trans*- and *cis*-PEP are shown in Fig. 1.

2.2. Equipment

The absorption spectra were recorded on a Varian Cary 1 Bio UV-Vis spectrophotometer (model 8452A) using 1 cm quartz cells and solute concentrations of $(1-3) \times 10^{-5}$ M. It has been verified that the Beer–Lambert law applies for the concentrations used. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with an F2T11 special configuration. The F2T11 special configuration of the Spex Fluorolog is designed to record simultaneously two emission scans (T-shape). It is particularly useful for anisotropy measurements. Each solution was excited near the absorption wavelength maximum using a 1 cm quartz cell and the concentration used for each derivative studied was $(1-3) \times 10^{-6}$ M giving absorbances always less than 0.1 to avoid any inner filter effect.

Fluorescence lifetimes were measured on a multiplexed time-correlated single photon counting fluorimeter (Edinburgh Instruments, model 299T). Details on the instrument have been published elsewhere [14]. The instrument incorporates an all-metal coaxial hydrogen flashlamp. Deconvolution analysis was performed by fitting over all the fluorescence decay including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, reduced χ^2 value, and Durbin–Watson (DW) parameters. The lifetime measurements were performed in argon-saturated solutions of the substrates at 298 K.

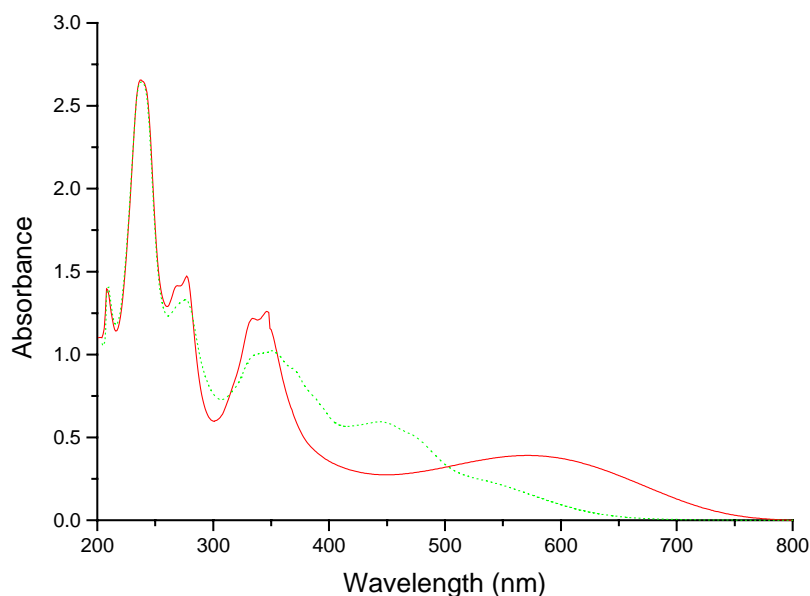


Fig. 2. Absorption spectra of *trans*-PEP (—) and *cis*-PEP (---) in THF.

3. Results and discussion

3.1. Absorption spectra of *trans*- and *cis*-PEP

The absorption spectra of *trans*- and *cis*-PEP in THF are shown in Fig. 2. The absorption spectrum of *trans*-PEP, which was already described in our recent paper [12], exhibits a peak at 336 nm that is attributed to the “free” pyrenes. Another peak at 346 nm has its origin in intramolecular interactions between adjacent pyrene units (associated pyrenes) along the polymer backbone. Finally, the broadband observed around 580 nm is caused by the polyacetylene chain, which indicates that the effective electronic conjugation is relatively long for this polymer. Indeed, results obtained from ZINDO/S calculations show that 10–12 coplanar repetitive units could reproduce the energy of this band [12].

The absorption spectrum of *cis*-PEP is much different from that observed for *trans*-PEP. Indeed, a new band appears at 453 nm. This clearly indicates that another kind of molecular interactions is formed for the *cis*-PEP. Moreover, the band observed around 580 nm in the absorption spectrum of *trans*-PEP is not observed for the *cis*-PEP but one can see a shoulder at 537 nm, which cannot be attributed to the absorption spectrum of associated pyrene units (see below). We believe that this band is due to the main polyacetylene chain, which indicates that the effective conjugation is shorter for the *cis* configuration of this polymer. To check this aspect, molecular mechanics calculations (MM2) [15] has been performed on *trans*-hepta(1-ethynyl-pyrene) and *cis*-octa(1-ethynyl-pyrene). The optimized geometries are represented in Fig. 3. One can see that, for the *trans* molecule, the main chain is well conjugated with pyrene units in almost a parallel orientation. On the other hand, steric interactions between pyrene units force the *cis* chain

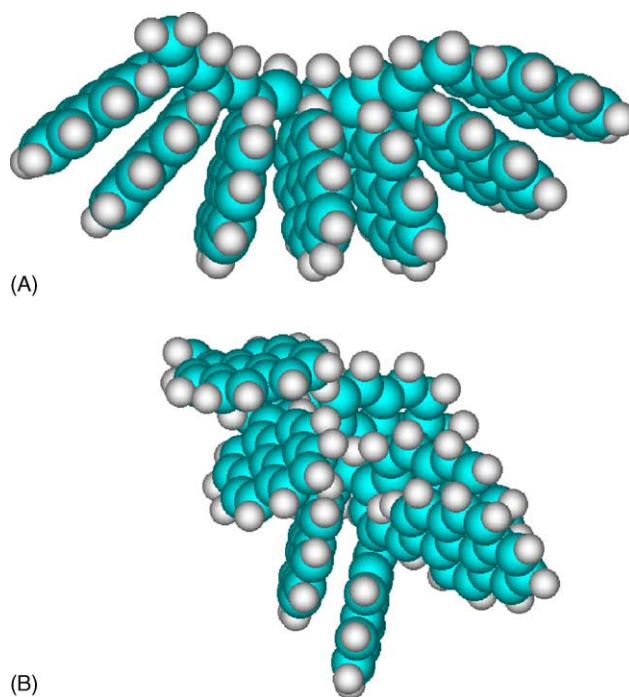


Fig. 3. Optimized geometry of *trans*-hepta(1-ethynyl-pyrene) (A) and *cis*-octa(1-ethynyl-pyrene) (B) by the MM2 method.

to twist out of plane, thereby reducing the effective conjugation.

3.2. Fluorescence spectra of *trans*- and *cis*-PEP

The fluorescence spectrum of *trans*-PEP, which has been described in our recent report [12], is illustrated in Fig. 4. This compound shows a band in the 360–465 nm region,

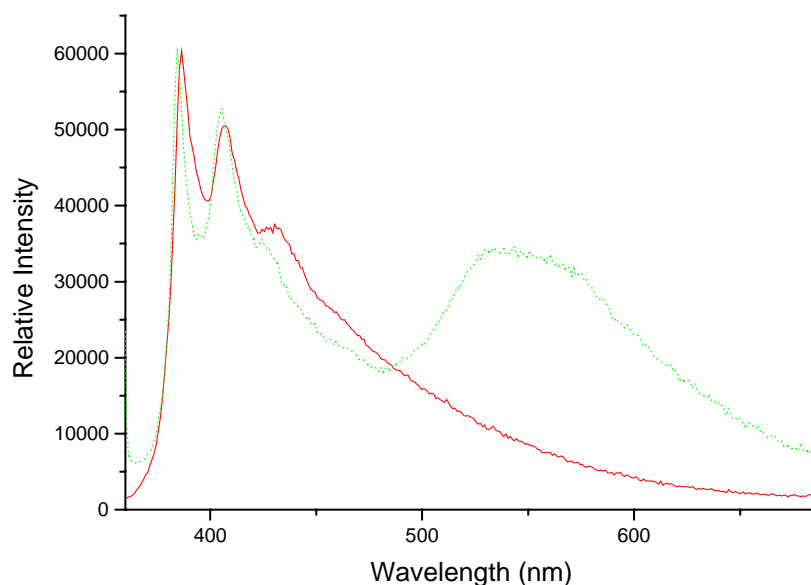


Fig. 4. Fluorescence spectra of *trans*-PEP (—) and *cis*-PEP (---) in THF.

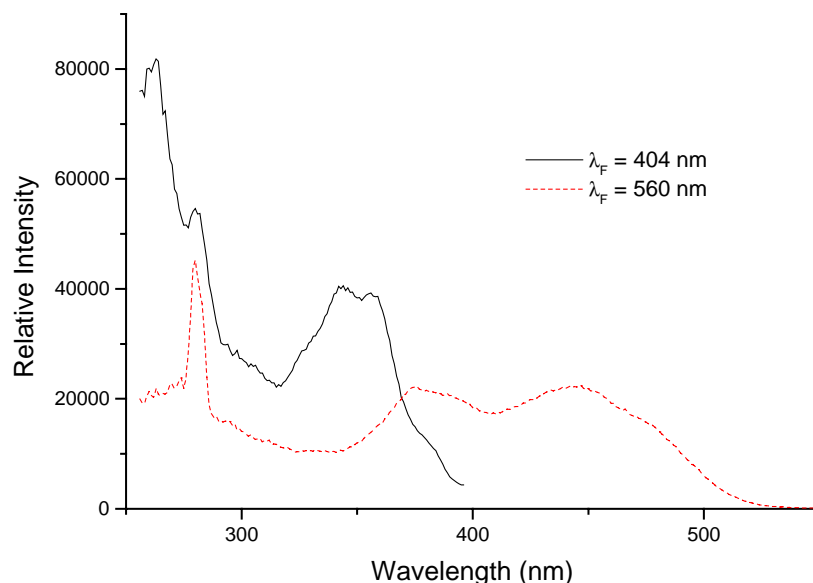


Fig. 5. Excitation spectra of *cis*-PEP monitored at $\lambda_F = 404$ nm (—) and at $\lambda_F = 560$ nm (---) in THF.

which is due to “free” pyrene units. The fluorescence spectrum of *trans*-PEP also shows an important emission intensity near 480 nm, a wavelength where pyrene itself does not emit. This has been interpreted in terms of the formation of a ground state complex between pyrene units [12]. The fluorescence spectrum of *cis*-PEP shows two distinct bands (Fig. 4). The first band, which exhibits vibronic peaks, is very similar to that observed for *trans*-PEP and could be attributed to “free” pyrene units. The broadband around 550 nm is interpreted in terms of the formation of intramolecular interactions between adjacent pyrene units along the molecular frame. Indeed, the same spectral properties described for di(1-ethynyl-pyrene) (DEP) [12] are observed for the fluorescence spectrum of *cis*-PEP. However, the spectral position of this band is much different from that observed for DEP ($\lambda_F \approx 480$ nm). This behavior could be explained by the different conformation adopted by the main chain in the *cis*-polymer. We believe that intrachain interactions may be formed by coiling of the main chain (as discussed above) giving rise to shorter distances for several pyrene units, and consequently to a large red-shift of the emission band.

In order to distinguish between the formation of an excited dimer or an excimer, the excitation spectra of *cis*-PEP have been measured at $\lambda_F = 404$ and 560 nm (Fig. 5). The excitation spectrum measured at $\lambda_F = 560$ nm is much different from that measured at $\lambda_F = 404$ nm. These results are not in favor of the formation of an excimer, which should have an excitation spectrum identical to that of the “free” pyrene units. The band centered at 385 nm and the large band around 446 nm should correspond to the shoulder at 365 nm and the band at 453 nm observed in the absorption spectrum of *cis*-PEP (Fig. 2). But the band observed at 537 nm in the absorption spectrum of *cis*-PEP is not observed in the excitation spectrum of this compound. This clearly shows that this band is not caused by the pyrene groups (associated

or not) and should involve the main polyacetylene chain as stated above.

3.3. Fluorescence decay profiles of *trans*- and *cis*-PEP

The fluorescence decay profiles of *trans*- and *cis*-PEP have been recorded at the pyrene fluorescence wavelength and at the pyrene–pyrene complex fluorescence wavelength (Fig. 6) and the results of the kinetic analysis are compiled in Table 1. The best fits obtained for these decays are complex and

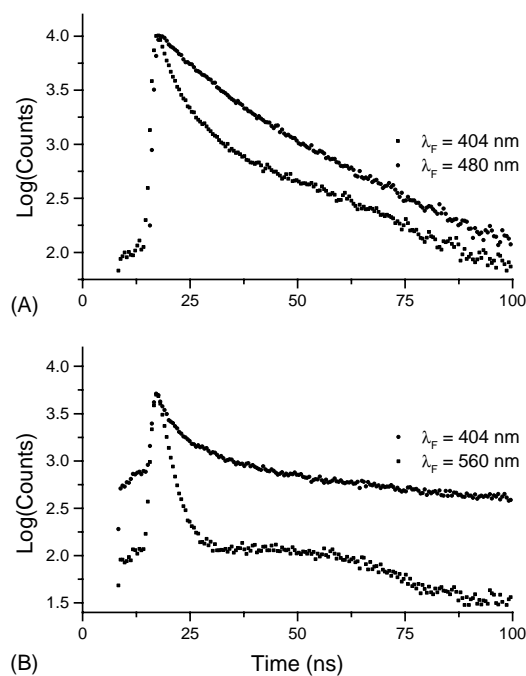


Fig. 6. Fluorescence decay profiles of *trans*-PEP (A) and *cis*-PEP (B) in THF.

Table 1
Fluorescence decay parameters of *trans*- and *cis*-PEP in THF at room temperature (298 K)

Molecule	λ_{exc} (nm)	λ_{F} (nm)	τ_{F} (ns)	B^a	f^b	χ^2
<i>trans</i> -PEP	346	404	$\tau_1 = 3.0^c$	$B_1 = 0.24$	0.06	1.40
			$\tau_2 = 12.9^c$	$B_2 = 0.73$	0.81	
			$\tau_3 = 59.8^c$	$B_3 = 0.03$	0.13	
			$\langle \tau_{\text{F}} \rangle = 18.3^d$			
	346	480	$\tau_1 = 1.5^c$	$B_1 = 0.71$	0.31	1.08
			$\tau_2 = 6.2^c$	$B_2 = 0.22$	0.38	
$\tau_3 = 17.8^c$			$B_3 = 0.07$	0.31		
		$\langle \tau_{\text{F}} \rangle = 8.4^d$				
<i>cis</i> -PEP	346	404	$\tau_1 = 0.2^c$	$B_1 = 0.95$	0.34	1.28
			$\tau_2 = 2.1^c$	$B_2 = 0.03$	0.15	
			$\tau_3 = 13.5^c$	$B_3 = 0.02$	0.51	
			$\langle \tau_{\text{F}} \rangle = 7.2^d$			
	346	560	$\tau_1 = 0.2^c$	$B_1 = 0.78$	0.32	1.18
			$\tau_2 = 1.4^c$	$B_2 = 0.21$	0.59	
$\tau_3 = 6.7^c$			$B_3 = 0.01$	0.09		
		$\langle \tau_{\text{F}} \rangle = 1.5^d$				

^a Normalized pre-exponential factor.

^b Fractional contribution to the total fluorescence intensity defined as:
 $f_i(\lambda) = B_i \tau_i / \sum_i B_i \tau_i$ [15].

^c Obtained from the reconvolution fit: $A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$.

^d Average lifetime calculated from the expression: $\langle \tau_{\text{F}} \rangle = \sum_i B_i \tau_i^2 / \sum_i B_i \tau_i$ [15].

involve a triexponential expression. The fluorescence decay recorded at the longer wavelength of each polymer does not show any rising component, which should be observed for an emission originating from an excimer [16]. Moreover, no negative component is calculated from the decay profile analysis. All these data rule out the formation of an excimer between the pyrene units of *trans*- and *cis*-PEP.

For both polymers, Table 1 indicates that the average lifetime measured at the longer wavelengths are significantly shorter than that measured at $\lambda_{\text{F}} = 404$ nm. This is a clear proof that a new species appear at longer wavelengths, which can be attributed to a static complex between the pendant pyrene units present in the polymer. It is worth pointing out that the fluorescence lifetime of “free” pyrene units are unusually low. Indeed, the fluorescence lifetime of the pyrene chromophore is normally quite high, reaching 400 ns in non-polar solvents [17]. Borsig and coworkers have however shown recently that pyrene chromophores grafted to polyethylene can have very short fluorescence lifetimes [18]. For instance, 1-pyrenylbutyl methacrylate (PyBMA) grafted to polyethylene, which has a fluorescence spectrum (385, 406 nm) very close to that of our polymers, has a lifetime of 13.3 ns [18].

Furthermore, the average fluorescence lifetime obtained at $\lambda_{\text{F}} = 404$ nm for *cis*-PEP is much shorter than that of *trans*-PEP measured at the same wavelength. This strongly suggests that pyrene units in the *cis*-polymer are in a different environment, probably by being closer to each other. This may happen, as discussed above, by coiling of the main

chain (Fig. 3B). Similarly, the average lifetime calculated at $\lambda_{\text{F}} = 560$ nm is shorter than that of *trans*-PEP, suggesting that this complex is stronger than that formed with pyrene units in *trans*-PEP. This is in agreement with the spectral positions of both complexes, indicating that the complex present in the *cis*-polymer is more stabilized.

4. Concluding remarks

The optical properties of *trans*- and *cis*-PEP in THF have been investigated. *trans*-PEP possesses an effective conjugation length, which is higher than that of *cis*-PEP. Both polymers show emissions originating from “free” pyrene units and associated pyrenes (pyrenes involved in intramolecular interactions along the polymer backbone). From excitation spectra and fluorescence decay profiles measured at the maximum of both fluorescence bands, it is shown that ground state interactions (static) are responsible for the long wavelength emissions observed. It is worth pointing out that the long-wavelength fluorescence band of *cis*-PEP is more stabilized, suggesting that pyrene units are closer to each other in this polymer.

The fluorescence decay profiles of both polymers are complex and are best fitted by a triexponential relation. It is observed that the average fluorescence lifetime of *cis*-PEP is much shorter than that of *trans*-PEP. We believe that stronger interactions between pyrene units (correlated to shorter intermolecular distances) in the *cis*-polymer are responsible for this behavior.

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