Synthesis, characterization and optical properties of novel well-defined di(1-ethynylpyrene)s

Javier Illescas, Carolina Caicedo, Gerardo Zaragoza-Galán, Yessica S. Ramírez-Fuentes, Adriana Gelover-Santiago, Ernesto Rivera[*]

Instituto de Investigaciones en Materiales Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510, Mexico, D.F., Mexico

ARTICLE INFO

ABSTRACT

Three di(ethynylpyrenes) were synthesized and characterized: (Z)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (DEPS), (E)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (DEPA) and 1,1′-(but-3-ene-1,3-diyl)dipyrene (DEPH). The optical properties of these oligomers were studied by absorption and fluorescence spectroscopies and the results were compared to those previously obtained for the related polymer *trans*-poly(1-ethynylpyrene) (*trans*-PEP). Intramolecular interactions occur between adjacent pendant pyrene units (associated pyrenes) in DEPS and DEPH, giving rise to static excimer emissions resulting from the stacking of aromatic rings. Excitation spectra jointly with life time fluorescence decays proved that such interactions take place in the ground state.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In the last 30 years, π-conjugated polymers have been regarded as promising materials for the development of several electronic devices such as light emitting diodes (LED's) [1–6], photovoltaic and solar cells [7], chromic devices [8], chemical sensors [9] and non-linear optical systems [10]. The opto-electronic properties vary remarkably depending on the degree of conjugation length between the consecutive repeat units. Among these materials, polyarylacetylenes have been widely studied by many research groups [11,12]. Arylacetylenes bearing non-polar groups are usually polymerized in the presence of WCl_6 and disubstituted acetylenes with $TaCl_5$ [13]. Masuda and co-workers reported the polymerization of several arylcetylenes bearing bulky condensed aromatic rings [14,15], and obtained polymers with molecular weights up to 140,000 g/mol, depending on the structure of the monomer. Surprisingly, many of these polymers showed to be highly conjugated in spite of their enhanced steric effects.

In a previous work, we reported the polymerization of 1-ethynylpyrene (EP), under different reaction conditions [16]. *Trans*-PEP and *cis*-PEP can be prepared selectively and the configuration of the obtained polymer depends in a big measure on the catalyst used in the synthesis. The preparation of these polymers is illustrated in Fig. 1. Catalytic polymerization of EP with WCl_6

resulted in the formation of *trans*-PEP with molecular weights ranging from 24,000 to 470,000 g/mol and polydispersities between 2.9 and 11 [16]. *Trans*-PEP showed to be highly conjugated exhibiting a maximum absorption wavelength at 580 nm in THF solution [17]. Molecular modeling showed that in his polymer the polyacetylene backbone adopts a nearly planar conformation and the pyrene pendants groups are oriented perpendicular to it, which causes an internal stacking of the aromatic groups. Furthermore, we studied the dependency of optical properties of poly(1-ethynylpyrene) in function of the polyacetylene backbone configuration and the internal stacking of the pendant groups [18,19]. Poly(1-ethynylpyrene) showed to be an appropriate model molecule because pyrene is an efficient fluorescent probe, which has been successfully used as a molecular label in the study of a huge variety of polymers [20–23,25]. It is very well known that pyrene has a long singlet lifetime and it readily forms excimers. The most relevant aspects of the photophysics of pyrene containing polymers have been the subject of some reviews [24,25].

Since it was difficult to elucidate the influence of the stacking on the optical properties of *trans*-PEP in absence of energy transfer phenomena, from the pyrene units to the conjugated polyacetylene backbone, we decided to synthesize three model dimers or di(1-ethynylpyrene)s (DEP) with short conjugation lengths: (Z)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (DEPS), (E)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (DEPA) and 1,1′-(but-3-ene-1,3-diyl)dipyrene (DEPH). The structures of these compounds are shown in Fig. 2. In the former, both pyrene units are placed in the same side of the butadiene chain; in the second, pyrene groups are

* Corresponding author. Tel.: +52 55 56 22 47 33; fax: +52 55 56 16 12 01.
E-mail address: riverage@iim.unam.mx (E. Rivera).

Fig. 1. Synthesis of *trans*-PEP and *cis*-PEP.
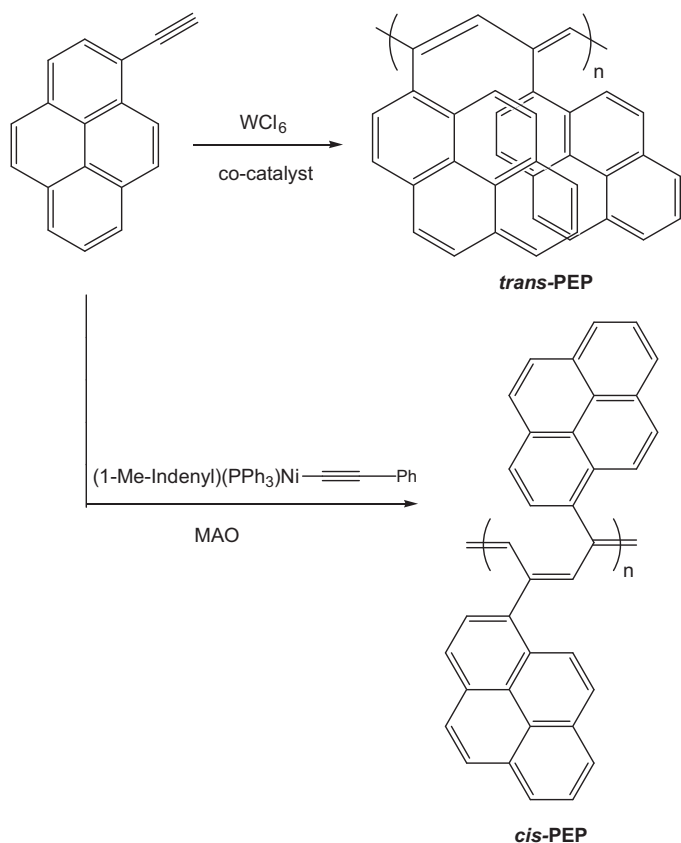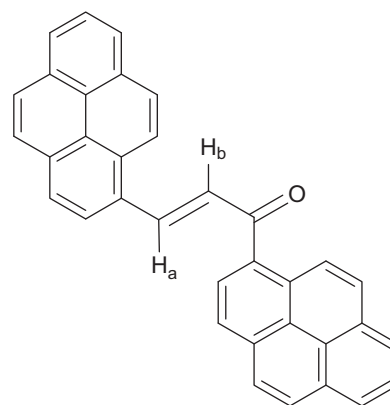

Fig. 2. Structure of the model dimers.

Scheme 1.

linked in opposite sides of the butadiene backbone and in the latter the double bond between both pyrene units was hydrogenated in order to allow free rotation of the pendant aromatic groups around the short backbone. Optical properties of these dimers were studied by UV–vis and fluorescence spectroscopies and the results were compared to those previously reported for *trans*-PEP [19].

2. Experimental

All the reagents involved in the synthesis were purchased from Aldrich and used as received. The solvents used in the reactions were purified by simple distillation. *Trans*-PEP and DEPS were prepared according to the methods previously reported by us [16]. The syntheses of the model dimers DEPH and DEPA is described in this section.

2.1. Synthesis of the dimers

(E)-1,3-di(pyren-1-yl)prop-2-en-1-one (**1**). A solution of 1-pyrenecarboxaldehyde (0.53 g, 2.3 mmol) and sodium hydroxide (0.08 g, 2 mmol) in ethanol (50 mL) was prepared. After 5 min, 1-acetylpyrene (0.5 g, 2.04 mmol) was added. The reaction mixture was heated to reflux for 4 h and then it was cooled to room temperature. The obtained product was separated by filtration, and then washed with water and ethanol. The crude product was purified by flash column chromatography using hexanes: ethyl acetate 1:2 as eluent. (E)-1,3-di(pyren-1-yl)prop-2-en-1-one (**1**) (0.7 g, 1.53 mmol) was obtained as a yellow solid. Yield: 70%.

IR (KBr): $\nu = 3036$ (=C–H stretching), 1728 (C=O), 1648, 1572 (C=C stretching), 1503 (C–H bending), 1370, 1241, 959, 837 (C=C–H out of plane bending), 750, and 702 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) (see Scheme 1): $\delta = 8.86$ (d, $J = 9$ Hz, H ortho of pyrene, 1H), 8.77 (d, $J = 9.2$ Hz, H′ ortho of pyrene), 8.45–7.98 (m, aromatic protons, 16H), 7.77 (d, $J = 15.6$ Hz, H^b, 1H), 7.73 (d, $J = 15.6$ Hz, H^a, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 195.76$ (C=O, s), 142.58(d), 134.29(d), 133.60, 133.25, 131.48(d), 131.39, 130.93(d), 130.86(d), 130.52(d), 129.76(d), 129.49(s), 129.42(s), 129.04(s), 128.99(s), 128.64(s), 127.56(s), 127.47(s), 126.64(t), 126.54(s), 126.38(s), 126.35(d), 126.24(d), 126.17(d), 125.34(d), 125.23(d), 125.16(s), 125.09(s), 124.76(d), 124.69(d), 124.51(t), 124.39 (d, 2C), 122.60 (d, 2C) ppm (aromatic and vinyl carbons). UV–vis (THF): $\lambda_{max} = 350$ nm. MS: m/z = 456 (M+), 255, 229, 226, 202,154 (BP), 136, 77, 65, and 51.

(E)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (**2**). A cold solution (0 °C) of methyl triphenyl posphonium iodide (0.44 g, 1.08 mmol) in THF (50 mL) was reacted with n-butyllithium (0.5 mL, 2.4 M in hexane, 1.2 mmol). After stirring for 30 min at 0 °C a mixture of **1** (0.5 g, 1.01 mmol) in THF was added. The reaction mixture was stirred at
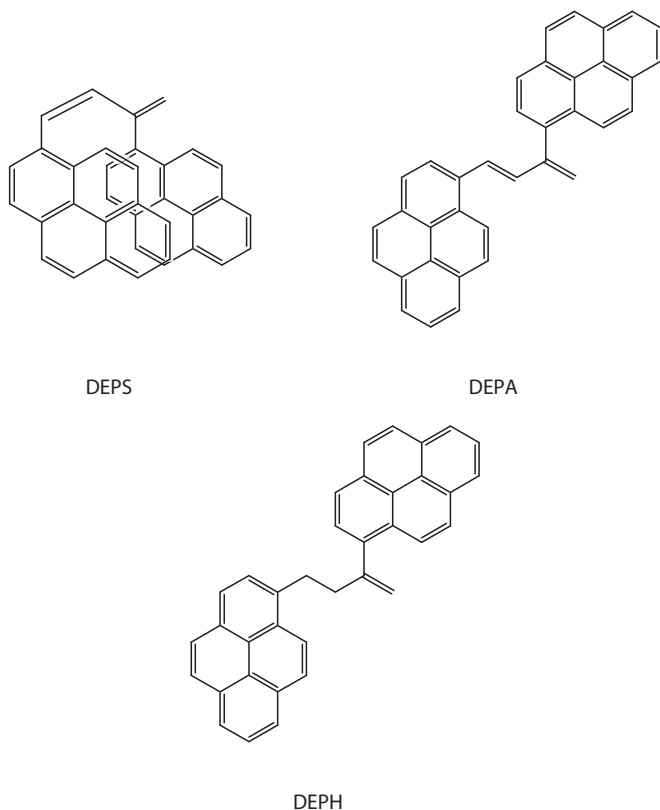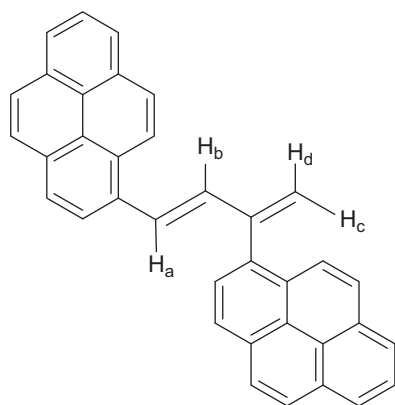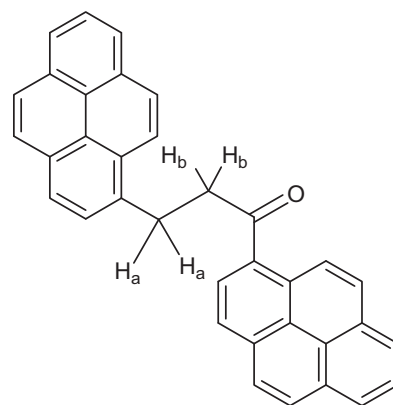
Scheme 2.

Scheme 3.

0 °C for 1 h, and then overnight at room temperature to complete reaction. A saturated aqueous NH_4Cl solution was added, and the reaction mixture was extracted with ether. The combined organic layers were washed with water and brine, dried with $MgSO_4$ and evaporated at reduced pressure. Purification of the residue by flash column chromatography using hexanes:ethyl acetate 1:4 as eluent gave anti-1,3-di(1-pyrenyl)-1,3-butadiene (**2**) (0.2 g, 0.44 mmol) as a light brown solid. Yield: 40%.

IR (KBr): ν = 3035 (=C–H stretching), 1598 (C=C stretching), 1582, 1485, 1456, 1430, 1415 (C–H bending), 1297, 1243, 1178, 1140, 1081, 838 (C=C–H out of plane bending), 754, 720, and 682 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) (Scheme 2): δ = 8.46 (d, J = 9.24 Hz, H ortho of pyrene, 2H), 8.24–8.04 (m, aromatic protons and H^a H^b, 18H), 6.01 (d, =CH$_2$, J = 1.23 Hz, H^c, 1H), 5.69 (d, J = 1.22 Hz, H^d, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 149.34(s), 145.43(s), 139.37(s), 137.03(s), 133.07(d), 132.21(s), 130.85 (s,s 2C), 130.7(d), 130.49(d), 130.48(s), 129.85(s), 129.71(d), 129.48(s), 129.25(d), 129.01(s), 128.83(s), 126.38(s), 127.21 (s), 127.01(d), 126.49(d), 126.22(d), 126.16(d), 126.09(d), 125.85(d), 124.64(d), 124.15 (d,d 2C), 123.56(d), 123.1(d), 122.61(d), 122.43(d), 122.3 (s,d, 2C), 114.87(d), 111.45 (t) (aromatic and vinyl carbons) ppm. UV–vis (THF): λ_{max} = 344 nm. MS: m/z = 454 (M+), 252, 227, 201, 154 (BP), 136, 77, 65 and 51.

1,3-di(pyren-1-yl)propan-1-one (**3**). **1** (0.25 g, 0.548 mmol), 10% of palladium on carbon (0.75 g), and ethyl acetate (350 mL) were stirred under hydrogen at room temperature for 3 days. Filtration through celite and removal of the solvent gave 1,3-dipyren-1-yl-propan-1-one (0.242 g, 0.528 mmol) of as yellow solid. Yield: 96%.

IR (KBr): ν = 3036 (=C–H stretching), 2938 (CH$_2$ stretching), 1729 (C=O), 1650, 1580 (C=C stretching), 1510 (C–H bending), 1380, 1315, 1241, 1211, 1119, 982, 836 (C=C–H out of plane bending), 749 and 705 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) (see Scheme 3): δ = 8.98 (d, J = 9.36 Hz, H ortho of pyrene, 1H), 8.37 (d, J = 9.2 Hz, H′ ortho of pyrene, 1H), 8.29–7.80 (m, aromatic protons, 16H), 3.96 (t, Hb, 2H), 3.79 (t, Ha, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 203.37 (s, C=O), 146.83(s), 142.29(s), 134.55(d), 133.04(s), 131.34(s), 131.25(s), 130.79(d), 130.25(s), 130.03(s), 130.00(d), 129.56(s), 128.42(d), 128.04(d), 127.85(d), 127.6(s), 127.47(s), 126.73(d), 126.11(d), 125.85(d), 125.76(d), 125.23(d), 125.02(s), 124.93(d), 124.35(s), 124.21(d), 124.02(d), 123.76(d), 123.13(s), 123.1(d), 122.64(d), 117.06(d), 113.33(s) (aromatic carbons), 44.47 (t, CH$_2$–C=O), 29.01 (t, CH$_2$-Pyrene) ppm. UV–vis (THF): λ_{max} = 340 nm. MS: m/z = 458 (M+), 255, 229, 215, 202, 154 (BP), 136, 77, 65 and 51.

1,1′-(but-3-ene-1,3-diyl)dipyrene (**4**). A cold (0 °C) solution of methyl triphenyl posphonium iodide (0.256 g, 0.633 mmol) in THF (50 mL) reacted with n-butyllithium (0.3 mL, 2.4 M in hexane, 0.72 mmol). After stirring at 0 °C for 30 min a mixture of **3** (0.242 g,

0.528 mmol) in THF was added. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 8 h in order to complete the reaction. A saturated aqueous NH_4Cl solution was added and the reaction mixture was extracted with ether. The combined organic layers were washed with water and brine, dried with $MgSO_4$ and evaporated. Purification of the residue by column chromatography, using hexanes:ethyl acetate 1:4 as eluent, afforded 1,1′-(but-3-ene-1,3-diyl)dipyrene (0.125 g, 0.274 mmol) as a yellow powder. Yield: 52%.

IR (KBr): ν = 3036 (=C–H stretching), 2938 (CH$_2$ stretching), 1596 (C=C stretching), 1581, 1483, 1455, 1432, 1417 (C–H bending), 1299, 1245, 1173, 1140, 1080, 839 (C=C–H out of plane bending), 752, 720, and 683 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) (see Scheme 4): δ = 8.4 (d, J = 9.2 Hz, H ortho of pyrene, 1H), 8.21–7.97 (m, aromatic protons, 16H), 7.82 (d, J = 9.15 Hz, H′ ortho of pyrene, 1H), 5.73 (d, J = 1.23 Hz, H^c, 1H), 5.33 (d, J = 1.5 Hz, H^d, 1H), 3.50 (t, H^b, 2H), 3.24 (t, H^a, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 155.98(s), 146.87(s), 141.87(s), 133.06(s), 132.49(d), 132.35(s), 131.36(s), 131.33(s), 131.25(s), 131.06(s), 130.25(s), 130.03(s), 129.7(d), 128.33(d), 127.85(d), 127.33(d), 126.73(d), 126.22(d), 126.2(d), 126.11(d), 125.89(s), 125.85(s), 125.45(s), 124.93(d), 124.22(d), 124.21(d), 124.04(d), 123.96(d), 123.56(d), 123.11(d), 121.45(s), 120.05(s), 115.58(d) (aromatic and vinyl protons), 114.32 (t, =CH$_2$), 37.31 (t, CH$_2$–C=), 34.59 (t, CH$_2$-Pyrene). UV–vis (THF): λ_{max} = 344 nm. MS: m/z = 456 (M+), 254, 229, 201, 154 (BP), 136, 77, 65 and 51.

Optimized geometries of all these dimers were estimated by DFT calculations using B3LYP/aug-cc-PVTZ(-f)//BHandH/G-31G* level of theory, taking into account the polarity of the solvent. For UV–vis and fluorescence spectroscopies, tetrahydrofuran (THF) was purchased from Aldrich (spectrophotometric grade). Prior to
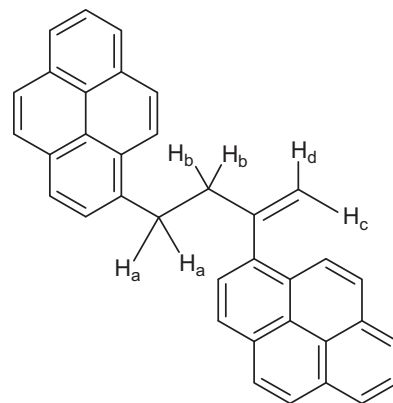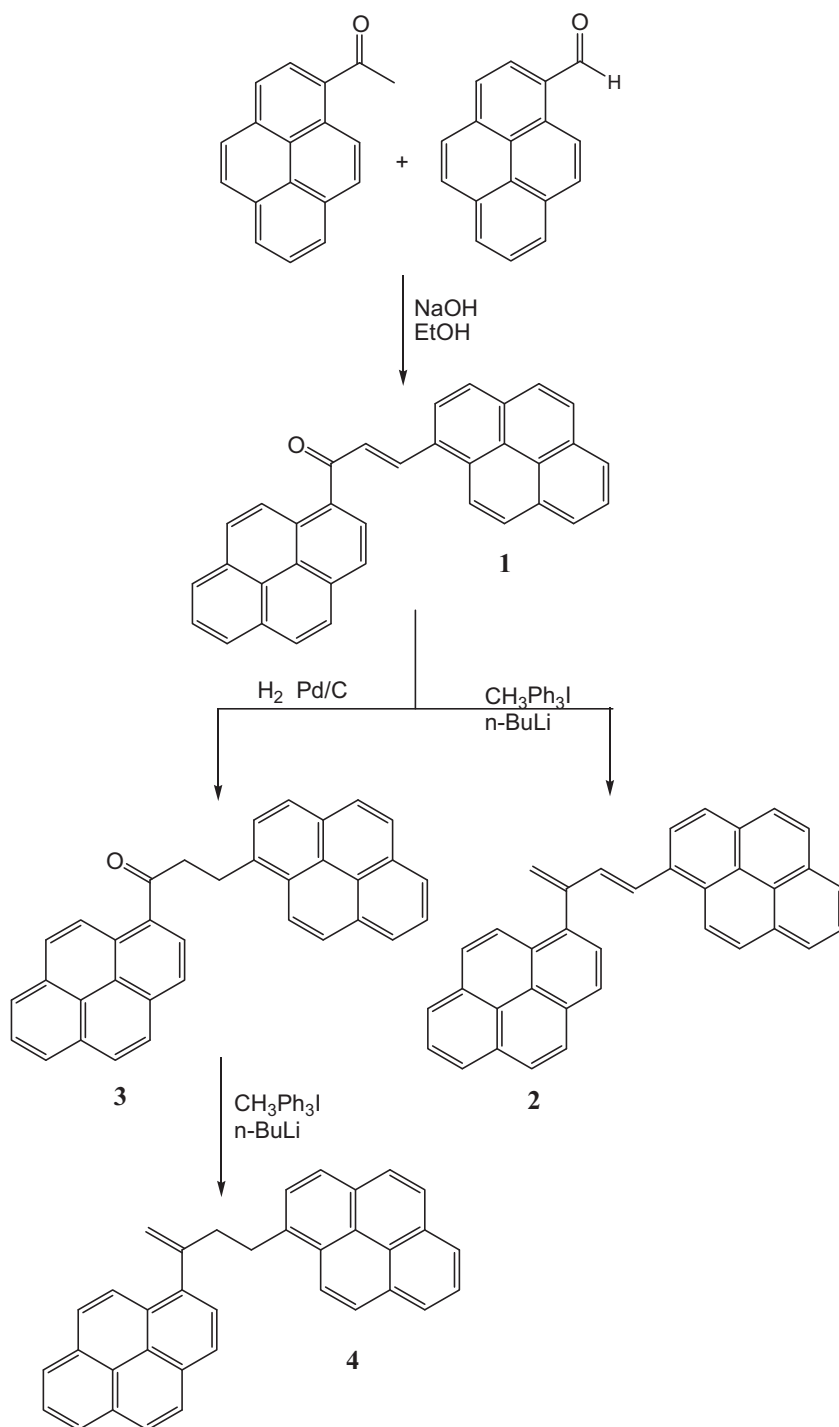

Scheme 4.

Fig. 3. Synthesis of DEPS, DEPA and DEPH.

use, the solvent was checked for spurious emission in the region of interest and found to be satisfactory. The absorption spectra in solution and in the solid state (cast film from THF solution) were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer (model 8452A) using 1 cm quartz cells and solute concentrations of 1–3×10^{-5} M for the polymer and the dimers. 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, which is designed to record simultaneously

two emission scans (T-shape). Each solution was excited near the absorption wavelength maximum using a 1 cm quartz cell. For polymer and dimers a concentration of about 1–3×10^{-6} M was used, giving absorbances of less than 0.1 in order to avoid any inner filter effect.

Fluorescence lifetimes were measured on a multiplexed time-correlated single photon counting fluorometer Edinburgh Instruments, model 299T with a resolution of 200 ps. The instrument incorporates an all-metal coaxial hydrogen flashlamp. Reconvolution analysis was performed by fitting over the entire
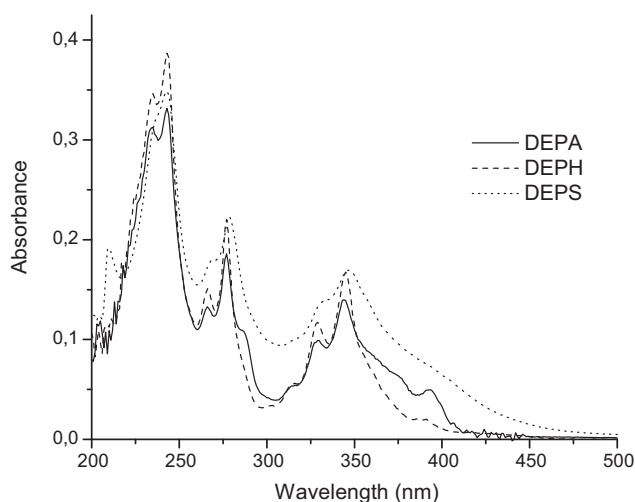
Fig. 4. Absorption spectra of the dimers.

fluorescence decay. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, the reduced χ^2 values, and Durbin–Watson (DW) parameters. The lifetime measurements were performed in argon-saturated solutions of the substrates at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of the dimers

The synthesis and characterization of trans-PEP and DEPS was previously reported by us [16]. DEPH and DEPA were prepared from 1-acetylpyrene according to the following synthetic sequence (Fig. 3).

1-Acetylpyrene and 1-pyrenecarboxaldehyde were reacted in the presence of NaOH in ethanol via a Claisen condensation to give (E)-1,3-di(pyren-1-yl)prop-2-en-1-one (**1**). This compound was reduced in the presence of hydrogen using Pd/C as catalyst to yield 1,3-di(pyren-1-yl)propan-1-one (**3**). Furthermore, **3** was reacted with CH_3Ph_3I in the presence of n-butyllithium via a Wittig reaction to give the desired dimer 1,1′-(but-3-ene-1,3-diyl)dipyrene (DEPH) (**4**). On the other hand, **1** was treated with the same reagents, under the same conditions as **3**, to produce the second desired dimer (E)-1,1′-(buta-1,3-diene-1,3-diyl)dipyrene (DEPA) (**2**). DEPH and DEPA were fully characterized by FTIR, ^{1}H- and ^{13}C NMR spectroscopies and the relevant spectroscopical data are included in the experimental section.

3.2. Absorption spectra of the dimers

The main purpose of this work is to study the nature of the pyrene–pyrene complexes present in the dimers. Particularly, we investigate the influence of butadiene chain geometry on the absorption and emission spectra of the dimers. Since these oligomers give rise to several pyrene–pyrene arrangements, their optical properties were measured in THF solution and compared with those previously reported for trans-PEP [16,19]. The absorption spectra of DEPS, previously reported in the literature [17] and those of DEPH and DEPA are shown in Fig. 4.

UV–vis spectra of the obtained dimers DEPS, DEPA and DEPH are very similar and show a well-defined band at $\lambda = 344$–346 nm, due to the $S_0 \rightarrow S_2$ transition of pyrene groups (Fig. 4). Moreover, DEPH, DEPA and DEPS exhibit a slight shoulder at $\lambda = 390$, $\lambda = 393$ nm and $\lambda = 396$ nm, respectively, which can be attributed

to the presence of pyrene–pyrene complexes. It is worth to point out that for pyrene, the $S_0 \rightarrow S_1$ band is very discrete and appears at $\lambda = 372$ in concentrated THF solutions [24], so that these shoulders arise from the presence of pyrene–pyrene intramolecular interactions.

According to Winnik [24], a clear indication of pyrene pre-association in the absorption spectrum is the broadening of the bands compared to systems where pyrene is molecularly dissociated. For 1-substituted pyrenyl compounds, the ratio P_A ($\lambda = 344$–346 nm)$= P_{peak}/P_{valley}$ is a useful parameter to know if there is pyrene association. If $P_A > 3$ there is no association of pyrene groups. This parameter was calculated for DEPS, DEPH and DEPA, giving values of 1.2, 1.5 and 1.6, respectively, thereby indicating the presence of pyrene–pyrene intramolecular interactions in all dimers, where the lower value was obtained for DEPS as expected. Moreover, DEPS exhibits a broadened red shifted absorption band ($\lambda = 346$ nm) compared to those showed by its homologues DEPH ($\lambda = 344$ nm) and DEPA ($\lambda = 344$ nm) (see Fig. 4), which reveals higher pyrene association in this dimer.

Comparing DEPS with its related polymer trans-PEP, we can observe that their absorption spectra in THF differ significantly [16]. Both compounds show an absorption band at $\lambda = 346$ nm, due to $S_0 \rightarrow S_2$ transition of pyrene units. However, trans-PEP exhibits an additional band at $\lambda_{max} = 580$ nm with cut off at $\lambda = 800$ nm, which is not perceived for DEPS (cut off at $\lambda = 600$ nm). This band is due to the highly conjugated polyacetylene sequences present in the polymer backbone. Previous molecular mechanics calculations (MM2), demonstrated that in trans-PEP the polymer backbone is well aligned with pendant pyrene units oriented perpendicular to it [16]. Thus, in trans-PEP pyrene groups adopt an almost parallel arrangement with regioregular stacking, where pyrene–pyrene distances vary between 3.1 and 4.5 Å.

3.3. Molecular modeling of the dimers

Optimized geometries of all dimers, taking into account the polarity of the solvent (THF), were obtained by molecular modeling, using DFT calculations. The most stable conformers for DEPS, DEPH and DEPA with their respective energy values are shown in Fig. 5. In fact, DEPA ($E = -1384.788186$ a.u.) (Fig. 5C), where pyrenes are placed in opposite sides of the butadiene chain, showed to be thermodynamically more stable than its homologue DEPS ($E = -1384.779399$ a.u.) (Fig. 5A). In this dimer, pyrenes are located in the same side of the butadiene chain, thereby overlapping. The average distance between pyrene units in DEPS was estimated to be 3.17 Å, very close to that estimated for trans-PEP (3.1 Å) [16,17].

On the other hand, DEPH exhibited two stable conformers energetically very close: in the first one pyrenes are placed on opposite sides of the butene chain ($E = -1386.003995$ a.u.) (Fig. 5B, left), whereas in the second one pyrenes are aligned, thus overlapping ($E = -1385.998462$ a.u.) (Fig. 5B, right). Even though the former conformer possesses a lower energy value, the latter fits better with the results obtained by fluorescence spectroscopy (vide infra). The average distance between pyrene units in this conformer is about 3.45 Å, higher than those estimated for DEPS and trans-PEP. This is due to the fact that in DEPH, pyrene chromophores are separated by three single bonds, which are longer than double bonds, thereby increasing the distance between these pendant aromatic groups. According to the energy values obtained by DFT calculations, from the thermodynamic point of view DEPH is the most stable dimer followed by DEPS and lastly by DEPA. However, regarding the pyrene–pyrene intramolecular interactions present in the dimers, fluorescence experiments revealed that the pyrene–pyrene complex present in DEPS is the strongest (vide infra).

A DEPS
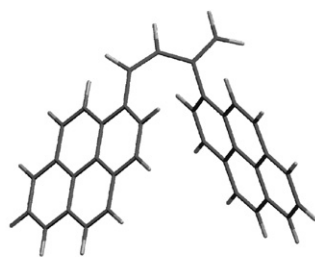
E = -1384.779399 a.u.

B DEPH
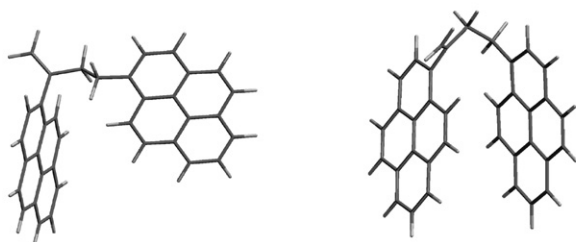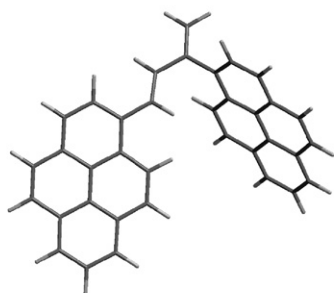

E = -1386.003995 a.u.   E = -1385.998462 a.u.

C DEPA

E = -1384.788186 a.u.

Fig. 5. Structures of the dimers obtained by molecular modeling.

Fig. 6. Fluorescence spectra of the dimers.

3.4. Fluorescence spectra of the dimers

Fluorescence spectra of the dimers in THF solution (Fig. 6) were previously reported by us in a *trans–cis* comparative study of polyarylacetylenes [19], however, in this article they are discussed in detail, focusing on the optical properties of the obtained dimers in function of their geometry.

Fluorescence spectra of DEPS, DEPA and DEPH, as well as that of *trans*-PEP [17,19], show broad emission bands between $\lambda_M = 360$–460 nm, due to excited non-associated pyrenes or "monomer emission". However, DEPS exhibits also a very intense excimer emission band at $\lambda_E = 480$ nm, resulting from intramolecular interactions between adjacent pyrene groups. Since DEPS possesses a rigid butadiene chain, where both pyrene groups are situated on the same side of the backbone, strong intermolecular pyrene–pyrene interactions occur. In this case, the rigidity of the chain restrains the mobility of the chromophores, thereby forcing them to stack.

Like DEPS, DEPH shows a broad monomer emission band at $\lambda_M = 391$ nm followed by an excimer emission at $\lambda_E = 498$ nm, due to the presence of intramolecular pyrene–pyrene interactions. Since in DEPH both pyrenes are linked by an aliphatic chain, they have no mobility restrictions and can freely rotate. Therefore, the pres-
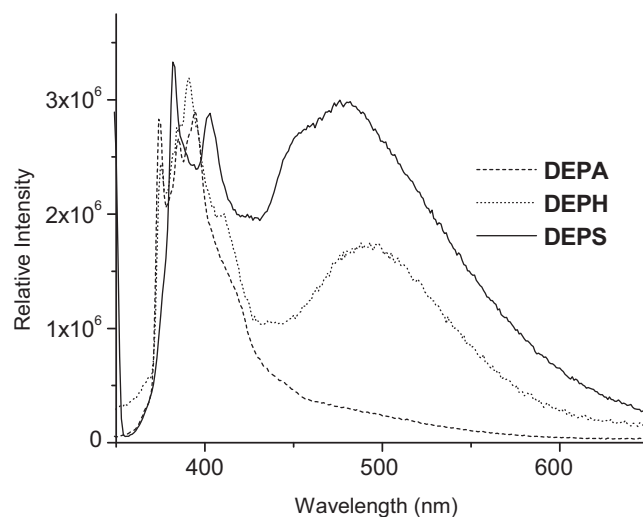
ence of an excimer emission in the fluorescence spectrum of this dimer, provide evidence that pyrene units have a natural tendency to stack in THF solution, giving rise to stable pyrene–pyrene complexes. Apparently, DEPA shows no excimer emission arising from pyrene–pyrene interactions, which can be explained in terms of the dimer geometry. In DEPA, pyrene chromophores are located in opposite sides of the rigid butadiene chain, so that they have to encounter by diffusion via a rotational process involving the single C–C bonds present in the molecule, in order to interact and give rise to an excimer emission.

Experimental intensity ratios (I_M/I_E) between the "monomer emission" band (I_M) and the excimer emission band (I_E) were found $I_M/I_E = 0.96$ and 1.84 for DEPS and DEPH, respectively. From these results, and based on the stereochemistry of the dimers and the distances between pyrene groups, DEPS exhibits higher efficiency of excimer formation than DEPH, as it could be expected. Therefore, such results are in agreement with the optimized geometries predicted by molecular modeling.

Regarding the pyrene–pyrene complexes present in polymers, it is worth to point out that the fluorescence spectrum of DEPS shows an intense excimer emission band at $\lambda_E = 480$ nm, whereas *trans*-PEP exhibits only moderate emission at the same wavelength. In fact, the highly conjugated backbone of *trans*-PEP ($\lambda_{max} = 580$ nm) [16] causes an auto-quenching effect over the excimer emission ($\lambda_E = 480$ nm) coming from the excited pyrene–pyrene complexes of this polymer. This is due to an energy transfer phenomenon, since the excimer emission band of *trans*-PEP and its maximum absorption band significantly overlap.

3.5. Excitation spectra and lifetime resolved fluorescence of the dimers

With the intention of elucidate the nature of the excimers, we recorded the excitation spectra of all dimers (Fig. 7). The excitation spectra provide evidence for ground state interactions of pyrenes. When the spectra are monitored at the monomer emission and the excimer emission, they are clearly different. Although both spectra can have similar overall features, they cannot be super-imposed [24]. Excitation spectra of DEPS, DEPH and DEPA recorded at λ_M of the "monomer emission" ($\lambda_M = 385$-390 nm) and at λ_E of the excimer emission ($\lambda_E = 480$ nm for DEPS, $\lambda_E = 492$ nm for DEPH) are different, which is against the rule of formation of a dynamic excimer [24]. Therefore, we have the presence of static excimers in
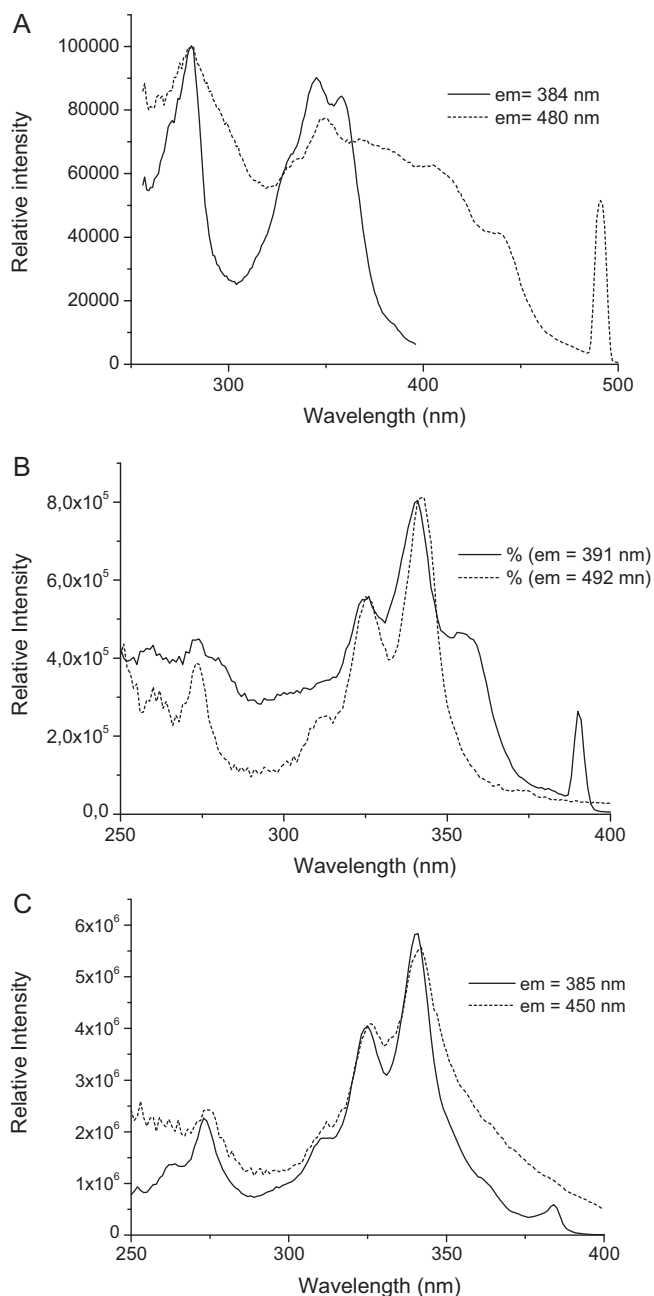
Fig. 7. Excitation spectra in THF of (a) DEPS; (b) DEPH; (c) DEPA.

reveal the presence of another kind of non-parallel pyrene–pyrene complexes resulting from other conformations arrangements that these sterically hindered dimers can adopt.

On the other hand, lifetime fluorescence experiments were recorded at λ_M of the "monomer emission" and at λ_E of the "excimer emission", in order to determine the average lifetime of dimers in the excited state and the results were compared to those previously observed for trans-PEP. The best fits obtained for these decays are complex and involve a triexponential expression since these dimers exhibit high steric effects and can adopt different conformations, which give rise to various emitting complexes (species). The fluorescence decays recorded at λ_E do not show any rising component, which should be observed for an emission originating from a dynamic excimer [24]. Moreover, no negative component is calculated from the decay profile analysis. All these data rule the formation of a static excimer between the pyrene units in these derivatives. It is worth pointing out that in the case of DEPS and trans-PEP the average lifetimes measured at λ_E are significantly shorter than those measured at λ_M. The results are summarized in Table 1.

According to these results, trans-PEP ($\tau_F = 18.3$ ns) and DEPS ($\tau_F = 18.2$ ns) exhibit similar lifetime values for pyrene units in the "non-associated" state [26,27], whereas DEPH ($\tau_F = 131.08$ ns) and DEPA ($\tau_F = 161.99$ ns), where pyrenes are more separated show longer lifetimes, closer to that of pyrene itself in CHCl$_3$ ($\tau_F = 132.6$ ns) [28]. This is due to the stereochemistry of the dimers, because in DEPH and DEPA pyrene units are farer from each other, while in DEPS and trans-PEP this separation is restricted by the configuration of the trans-transoidal insaturated backbone.

Concerning intramolecular interactions, apparently no excimer emission was observed for DEPA, where pyrenes are placed in opposite sides of the butadiene chain. However pyrene association was detected in the absorption spectrum ($P_A = P_{peak}/P_{valley}$) and the quantum yield of this compound in THF was measured relative to an anthracene standard and was estimated to be $\varphi = 0.91$. Alternatively in DEPS, pyrene units in the associated state (static excimer emission) exhibit a very short average lifetime ($\tau_F = 3.3$ ns), even shorter than that measured for trans-PEP ($\tau_F = 8.4$ ns). Borsig and co-workers reported similar fluorescence lifetimes for pyrene chromophores grafted to polyethylene [27]. For instance, 1-pyrenylbutyl methacrylate (PyBMA) grafted to polyethylene, which has a fluorescence spectrum (385 nm, 406 nm), has a lifetime of 13.3 ns, very close to that of DEPS and trans-PEP in the "non-associated" state [16]. By contrast, lifetime for pyrene complexes (static excimer emission) in DEPH ($\tau_E = 96.52$ ns) is much longer that those measured for DEPS and trans-PEP. Kamat et al. reported similar lifetimes for the excimer emission of poly(1-vinylpyrene) ($\tau_E = 110$ ns) in the same solvent used in our study (THF) [28]. This phenomenon can be explained in terms of the distance between pyrene units, because in poly(1-vinylpyrene) pyrenes are linked to a totally saturated aliphatic backbone. Previous MM2 calculations carried out in short segments of trans-PEP confirmed that the average distance between pyrene units was 3.5 Å [16].

As we can see, the static excimer lifetime in DEPS is shorter than in DEPH. DFT calculations carried out in our dimers showed that the average distances between pyrene units were 3.17 and 3.45 Å for DEPS and DEPH respectively. In DEPS pyrene–pyrene interactions are much stronger and permanent because the distance between the chromophores is shorter and steric restrictions force them to interact, whereas in DEPH the distance between pyrene units is longer and the saturated chain allows pyrenes to rotate and adopt more relaxed conformations, where pyrenes are farer to each other. The closer the pyrene units are in the dimer, the shorter the lifetime is; consequently shorter lifetimes reveal that these pyrene complexes are strong and highly stabilized.

all these dimers, as it was found in trans-PEP [18]. On the other hand, for these compounds the excitation spectra monitored at the excimer emission show red shifted and broadened bands, compared to those of the spectra monitored at the monomer emission. For instance, for DEPS ($\lambda_{(M)} = 346$, $\lambda_{(E)} = 350$), DEPH ($\lambda_{(M)} = 340$, $\lambda_{(E)} = 342$), and DEPA ($\lambda_{(M)} = 340$, $\lambda_{(E)} = 342$), so that we can conclude that DEPS possesses a higher degree of pyrene association than the other dimers.

In the particular case of DEPS, we can observe a big difference between both excitation spectra, since that recorded at the monomer emission resembles to the absorption spectrum, whereas that recorded at the excimer emission exhibited a very broadened red shifted band with the presence of shoulders at 410 and 440 nm. This broadening results from the extremely tight stacking of the pyrene chromophores in this dimer. We believe that the presence of shoulders, which are not observed in the absorption spectrum,

Table 1
Fluorescence lifetime decay parameters for the dimers and trans-PEP.

Compound	λ_{exc} (nm)	λ_{em} (nm)	Lifetime (ns)	B^b	f^c	χ^2
trans-PEP	346	404	$\tau_1{}^a = 3.0$ $\tau_2{}^a = 12.9$ $\tau_3{}^a = 59.8$ $\langle\tau_F\rangle^d = 18.3$	$B_1 = 0.24$ $B_2 = 0.73$ $B_3 = 0.03$	0.06 0.81 0.13	1.40
tail (excimer)	346	480	$\tau_1{}^a = 1.5$ $\tau_2{}^a = 6.2$ $\tau_3{}^a = 17.8$ $\langle\tau_F\rangle^d = 8.4$	$B_1 = 0.71$ $B_2 = 0.22$ $B_3 = 0.07$	0.31 0.38 0.31	1.08
DEPS	345	382	$\tau_1{}^a = 1.07$ $\tau_2{}^a = 7.13$ $\tau_3{}^a = 26.2$ $\langle\tau_F\rangle^d = 18.2$	$B_1 = 0.40$ $B_2 = 0.41$ $B_3 = 0.19$	0.052 0.352 0.569	1.40
(excimer)	345	482	$\tau_1{}^a = 0.41$ $\tau_2{}^a = 2.29$ $\tau_3{}^a = 6.9$ $\langle\tau_F\rangle^d = 3.3$	$B_1 = 0.54$ $B_2 = 0.40$ $B_3 = 0.06$	0.142 0.581 0.276	1.02
DEPA	345	391	$\tau_1{}^a = 2.639$ $\tau_2{}^a = 13.28$ $\tau_3{}^a = 168.45$ $\langle\tau_F\rangle^d = 161.99$	$B_1 = 0.06$ $B_2 = 0.32$ $B_3 = 0.61$	0.002 0.039 0.959	1.51
DEPH	345	391	$\tau_1{}^a = 146.00$ $\tau_2{}^a = 17.77$ $\tau_3{}^a = 4.43$ $\langle\tau_F\rangle^d = 131.08$	$B_1 = 0.42$ $B_2 = 0.40$ $B_3 = 0.18$	0.886 0.102 0.012	1.51
(excimer)	345	492	$\tau_1{}^a = 128.29$ $\tau_2{}^a = 2.88$ $\tau_3{}^a = 68.76$ $\langle\tau_F\rangle^d = 96.52$	$B_1 = 0.30$ $B_2 = 0.07$ $B_3 = 0.63$	0.469 0.003 0.528	1.59

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

[b] Normalized pre-exponential factor.

[c] Fractional contribution to the total fluorescence intensity: $fi(\lambda) = B_i\tau_i/\sum_i B_i\tau_i$.

[d] Average lifetime calculated from the expression: $\langle\tau_F\rangle = \sum_i B_i\tau_i^2/\sum_i B_i\tau_i$.

4. Conclusion

Fluorescence experiments carried out in model dimers confirmed that it is necessary for pyrene units to be in the same side of the polymer backbone to generate static excimer emissions. The presence of double bonds restrains the mobility of pyrene units, thereby favoring the formation of complexes. However, when two pyrenes are linked by a saturated propane chain, the aromatic groups have a natural tendency to stack. According to the intensity of the excimer emissions of the different dimers, DEPS exhibited a stronger pyrene–pyrene interactions than trans-PEP and DEPH. Pyrene–pyrene complexes in DEPH exhibited a similar lifetime to that observed in poly(1-vinylpyrene).

References

[1] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.C.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lgdlung, W.R. Salanek, Nature 397 (1999) 121.
[2] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed. Eng. 37 (1998) 402.
[3] M.T. Bernius, M. Inbasekaran, J. O'Brien, W.S. Wu, Adv. Mater. 12 (2000) 1737.
[4] A.C. Grimsdale, K.L. Chan, R.E. Martin, P.G. Jokisz, A.B. Holmes, Chem. Rev. 109 (2009) 897.
[5] L. Akcelrud, Prog. Polym. Sci. 28 (2003) 875.
[6] D.Y. Kim, H.N. Cho, C.Y. Kim, Prog. Polym. Sci. 25 (2000) 1089.
[7] Y.J. Cheng, S.H. Yang, C.S. Hsu, Chem. Rev. 109 (2009) 5868.
[8] P.M. Beaujuge, J.R. Reynolds, Chem. Rev. 110 (2010) 268.
[9] S.W. Thomas, G.D. Joly, T.M. Swager, Chem. Rev. 107 (2007) 1339.
[10] M.J. Cho, D.H. Choi, P.A. Sullivan, A.J.P. Akelaitis, L.R. Dalton, Prog. Polym. Sci. 33 (2008) 1013.
[11] J.Z. Liu, J.W.Y. Lam, B.Z. Tang, Chem. Rev. 109 (2009) 5799.
[12] B.Z. Tang, X.X. Kong, X.H. Wan, X.D. Feng, Macromolecules 30 (1997) 5620.
[13] T. Masuda, H.J.M.S. Tavhimori, Pure Appl. Chem. A 31 (1994) 1675.
[14] T. Masuda, S.M.A. Karim, R. Nomura, J. Mol. Catal. A 160 (2000) 125.
[15] S.M.A. Karim, K. Musikabhuma, R. Nomura, T. Masuda, Proc. Jpn. Acad. Ser. B 99 (1999) 7.
[16] E. Rivera, R. Wang, X.X. Zhu, D. Zargarian, R. Giasson, J. Mol. Catal. A 204–205 (2003) 325.
[17] E. Rivera, M. Belletête, X.X. Zhu, G. Durocher, R. Giasson, Polymer 43 (2002) 5059.
[18] M. Belletête, E. Rivera, R. Giasson, X.X. Zhu, G. Durocher, Synth. Met. 143 (2004) 37.
[19] E. Rivera, M. Aguilar-Martínez, G. Terán, R. Flores, J.A. Bautista-Martínez, Polymer 46 (2005) 4789.
[20] S. Piçarra, P. Relogio, C.A.M. Alfonso, J.M.G. Martinho, J.P.S. Farinha, Macromolecules 36 (2003) 8119.
[21] J. Duhamel, S. Kanagalingam, T.J. O'Brien, M.W. Ingratta, J. Am. Chem. Soc. 125 (2003) 12810.
[22] K. Miyazawa, F.M. Winnik, J. Phys. Chem. B 107 (2003) 10667.
[23] K.D. Berglund, T.M. Przybycien, R.D. Tilton, Langmuir 19 (2003) 2705.
[24] F.M. Winnik, Chem. Rev. 93 (1993) 587.
[25] J. Duhamel, Acc. Chem. Res. 39 (2006) 953.
[26] M. Sarobe, J.W. Zwikker, J.D. Snoeijer, U.E. Wiersum, L.W. Jenneskens, J. Chem. Soc. Chem. Commun. (1994) 89.
[27] M. Danko, P. Hrdlovic, E. Borsig, J. Macromol. Sci. Pure Appl. Chem. A 38 (2001) 467.
[28] P.V. Kamat, R. Basheer, M.A. Fox, Macromolecules 18 (1985) 1366.