

# Synthesis of Ionic Polyurethanes with Pyrene Rings: Spectral Properties and Fluorescence Quenching Study

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**ABSTRACT:** Hydrophilic ionic polyurethanes with 4-chloromethylphenylcarbamoyl-1-oxymethylpyrene located on the quaternary ammonium structure from a polymer based on poly(ethylene glycol), isophorone diisocyanate, and *N*-methyldiethanolamine were prepared by a quaternization reaction, in which the amount of pyrene covalently attached to the polymeric backbone ranged from 1.14 to 19.82 mmol of fluorophore/100 g of polymer. It was interesting to compare the photoluminescence of the pyrene polyurethane carrying a few mole percent of pyrene moieties with that of a third polymer resulting from its subsequent quaternization with benzyl chloride up to a concentration of ionic groups as in the latter (quaternization degree = 14.15%). The process of excimer formation between the pyrene molecules attached to the ionic polyurethane was investigated in tetrahydrofuran (THF), dimethylformamide, film, and THF/H<sub>2</sub>O to illustrate the expected differences in the polymer behavior compared with that of the starting pyrene derivative. The formation of aggregates or core-shell micelles was sustained by the fluorescence data, which indicated the existence of pyrene units in the ground state of the molecule, giving rise thus to an explanation for the high excimer-to-monomer intensity ratio. The fluorescence decay of pyrene polyurethanes in the presence of various concentrations of nitrobenzene used as a quencher was analyzed too when the fluorescence quenching in the polymer solution normally followed Stern–Volmer kinetics. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 3945–3956, 2005

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## INTRODUCTION

The design of photosensitive materials containing an aromatic fluorophore moiety highly sensitive to an external stimulus occupies a central

place in the development of functional devices for various specialized applications, including chemosensing, optical switching, and molecular computation.<sup>1–3</sup> Of the many promising fluorophores, the investigation of the photophysical properties of the (non)-covalently bound pyrene chromophore in light-sensitive molecular structures is among the most exciting, and as a result, intense research activity has been devoted to this subject.<sup>4–6</sup> A topic of particular

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interest continues to be the study of the nature of polymer micellization in fluorescently pyrene-labeled polymers,<sup>7,8</sup> amphiphilic block copolymers,<sup>9</sup> and polyelectrolyte systems<sup>10,11</sup> to provide information on the structure, microscopic dynamics, and conformational properties of the associative (bio)polymers in solution.<sup>12</sup> An extension of this methodology to the study of some acrylic and Nafion ionomer membranes with pyrene and its cationic derivatives as lumiphoric structural units has added significant structural details to the recent models for the self-assembly of ionomeric chains, which were previously deduced from complementary methods.<sup>13–15</sup> Although there is a great need for new and improved approaches for the fabrication of sensing films in the detection of various chemical and biological analytes, it is surprising that just a few studies have investigated polyurethanes of the ionomeric/nonionomeric type, whose excellent properties are well known. Pyrene as a free fluorescent probe in such polymers usually is used for the evaluation of the polarity of cellular membranes,<sup>16</sup> the hydrophobicity of polyurethane foams,<sup>17</sup> or the interactions in solutions of model polyurethane ionomers.<sup>18</sup> In other work,<sup>19</sup> the number of hydrophobic substituents for a set of hydrophobically modified ethoxylated urethane polymers with C<sub>16</sub>H<sub>33</sub> end groups was determined with pyrene as a fluorescent probe.

Therefore, the main motivation for this work is to broaden the platform of photoreactive coatings through the preparation of new polyurethane ionomers with pyrene pendants covalently attached to polymers to evaluate and eventually improve the sensitivity of the resulting materials. Previously, we have focused our attention on photoionomers with fluorescent, photochromic, or UV/laser ablative properties generated from stilbene,<sup>20,21</sup> azoaromatic,<sup>22–24</sup> and triazene moieties<sup>25,26</sup> located in the hard or soft segments of the polyurethane backbone. In this article, we describe the synthesis, characterization, and fluorescence of ionic polyurethanes in which the hydrophobic pyrene is linked to the quaternary ammonium structure of the polymeric backbone, which contains hydrophilic sequences of poly(ethylene oxide) as the soft segment. The effect of the variation of the pyrene content on the photophysical properties of the polymers is discussed, and a fluorescence quenching study of polyurethane-linked pyrene by nitrobenzene was also performed to

assess the accessibility of the fluorophore to neutral molecules in a tetrahydrofuran (THF) solution.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) [PEG; number-average molecular weight ( $M_n$ ) = 2000; Aldrich] was dried and degassed at 80 °C and 1–2 mmHg for 2 h before utilization. Isophorone diisocyanate (IPDI; Aldrich) and *N*-methyldiethanolamine (NMDA; Aldrich) were used as received. Dimethylformamide (DMF) was dried over 5-Å molecular sieves.

### Pyrene Derivative Synthesis: 4-Chloromethylphenylcarbamoyl-1-oxymethylpyrene (Py-QA)

A solution of 4-chloromethylphenylisocyanate (1.44 g, 8.6 mmol) in 10 mL of anhydrous DMF was dropwise added to a solution of 1-pyrenemethanol (2 g, 8.62 mmol) in 20 mL of DMF; this was followed by stirring at 65 °C for 7 h under a nitrogen atmosphere. After the removal of DMF, the crude product was recrystallized from DMF/THF (1:1 v/v).

Yield: 3.16 g (92%) of red-brown crystals. ELEM. ANAL. Calcd. for C<sub>25</sub>H<sub>18</sub>ClNO<sub>2</sub>: C, 75.09%; H, 4.50%; Cl, 8.88%; N, 3.50%. Found: C, 75.0%; H, 4.47%; Cl, 8.80%; N, 3.48%. <sup>1</sup>H NMR [dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>),  $\delta$  ppm]: 4.53 (s, 2H, CH<sub>2</sub>Cl), 5.4 (s, 2H, CH<sub>2</sub>OCONH), 7.28–7.38 (m, 4H, aromatic protons), 7.96–8.38 (m, 9H, pyrene), 9.4 (s, 1H, NHCOO). IR (KBr, cm<sup>-1</sup>): 1700 (CO), 1600 (aromatic CH), 820, 710 (pyrene), 3350 (urethane NH). UV (CH<sub>3</sub>OH): 275, 311, 328, 345 nm.

### Polymer Synthesis

The polyurethane precursor (PU-PR) was synthesized by a two-step condensation reaction from poly(ethylene oxide) diol (PEO;  $M_n$  = 2000, 0.01 mol), IPDI (0.06 mol), and NMDA (0.05 mol). The NCO-terminated prepolymer was prepared by the reaction of IPDI with PEO in the presence of dibutyltin dilaurate (0.03 wt % in toluene, based on total solids) under a dry argon atmosphere at 60 °C for 6 h. After the prepolymer was degassed *in vacuo* and its temperature was reduced at 50 °C, NMDA in anhydrous acetone was added. The reaction was car-

ried out at 55–60 °C for 4 h. The pyrene rings were introduced by a partial quaternization of the aforementioned polyurethane (1.5 g of PU-PR) with 0.3 mmol of the pyrene derivate (Py-PUC1) or 0.0165 mmol (Py-PUC2) according to the procedure described previously.<sup>20</sup> Similarly, another polymer (Py-PUC3) with about the same content of ionic groups as that of Py-PUC1 was obtained by the quaternization of 1 g of Py-PUC2 with benzyl chloride (0.2 mmol). All polymers were precipitated in diethyl ether, collected by filtration, and then dried under reduced pressure.

### Measurements

The structures of the monomers and polymers were verified by <sup>1</sup>H NMR and IR/ultraviolet-visible (UV-vis) spectroscopy with a Bruker 400-MHz spectrometer and Specord M80 and M42 spectrophotometers, respectively. The molecular weight distribution of the precursors (PU-PR) was measured with a PLEMD 950 apparatus equipped with two PLgel mixed columns (weight-average molecular weight = 26,500). The reduced viscosity of PU-PR (0.27 dL g<sup>-1</sup>) was determined at 25 ± 0.2 °C in a DMF solution (concentration = 0.4 g dL<sup>-1</sup>) with an Ubbelohde viscometer with a 0A capillary. The concentration of pyrene was estimated from the NMR spectrum, whereas the ionic groups were calculated from the ionic chlorine (Py-PUC1 and Py-PUC3). Differential scanning calorimetry (DSC) analysis for nonionic polyurethane over the temperature range of -130–230 °C was recorded at a heating rate of 20 °C min<sup>-1</sup> with a PerkinElmer differential scanning calorimeter. The polymer film was prepared by the casting of the polymer solution in DMF (concentration = 1 wt %) onto quartz plates and then was allowed to dry at 50–55 °C under reduced pressure. For fluorescence studies, it was necessary to remove the unattached pyrene present in the polymer by successive precipitation into diethyl ether, followed by drying *in vacuo*. The fluorescence spectra were obtained at room temperature (without corrections) with an SLM 8000 spectrofluorimeter (Japan) containing a double monochromator with a diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type, and a selective amplifier, as presented earlier.<sup>20</sup>

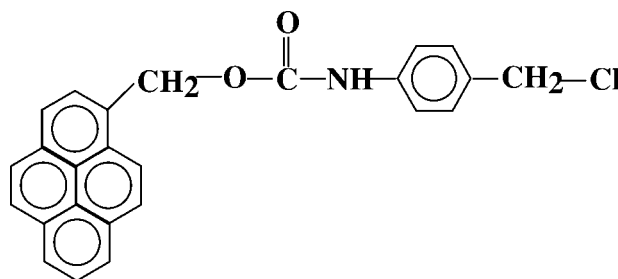
UV (DMF) for Py-PUC1: 275, 296, 313, 326.5, 345.5 nm.

## RESULTS AND DISCUSSION

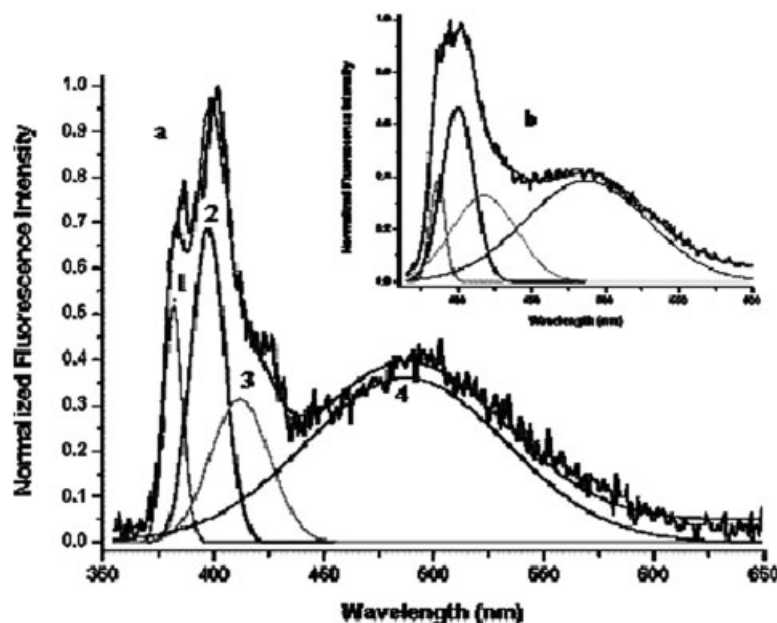
The investigation of a chromophoric derivative in which the steric hindrance generated by the pyrene rings is suppressed through a spacer group could contribute to a better understanding of the photoinduced properties in polyurethanes as the pyrene is attached to the polymer chain. For this reason, a highly reactive halide containing 1-substituted pyrene moieties was prepared from a postcoupling reaction of 1-pyrenemethanol with 4-chloromethylphenylisocyanate. The structure of Py-QA is depicted in Scheme 1. The pyrene derivative was characterized with spectral and analytical methods. The results of elemental analysis given in the Experimental section were in agreement with the calculated values of the assumed structure.

### UV-vis and Fluorescence Spectroscopy of the Pyrene Derivative

Because the fluorescence data have indicated that on excitation pyrene strongly emits as both a monomer and an excimer,<sup>27</sup> we carried out a study on substituted pyrene to distinguish between the mentioned possibilities and to measure the intensity ratio of the excimer emission maximum to the monomer emission maximum ( $I_E/I_M$ ) by taking the integrals under the fluorescence peaks. Consequently, a steady-state emission spectrum of pyrene derivative was recorded in DMF and THF solutions with two excitation wavelengths of 344 and 365 nm. The vibronic fluorescence spectrum of Py-QA in DMF shows four peaks centered at 384.5 ( $I_1$ ), 400.8 ( $I_2$ ), 420 ( $I_3$ ), and 487.2 nm ( $I_4$ ) and corresponding to allowed vibrations and forbidden vibrations, including the 0–0 band [Fig. 1(a)]. The fluorescence intensity of the  $I_1$ – $I_3$  peaks originates from the single fluorophore molecular emission, whereas the intensity of the  $I_4$  peak



**Scheme 1.** Structure of the pyrene derivative (Py-QA).



**Figure 1.** Deconvolution results of the fluorescence spectra of the pyrene derivative in DMF, monitored (a) at  $\lambda_{\text{exc}} = 344$  nm and (b) at  $\lambda_{\text{exc}} = 365$  nm: (1–3) monomer fluorescence and (4) excimer fluorescence.

corresponds to an excimer emission resulting frequently from the encounter between an excited pyrene and a pyrene molecule in its ground state or from the direct excitation of aggregates (dimers). As expected, the vibrational structure of the fluorescence of Py-QA under the same conditions is well preserved in absorption and emission spectra. When the spectrum was recorded at a higher excitation wavelength ( $\lambda_{\text{ex}} = 365$  nm), the position of the maximum of the fluorescence spectrum [Fig. 1(b)], centered at 386.2 and 417.5 nm, respectively, was slightly shifted toward red ( $I_1$ ) or blue ( $I_3$ ). To determine precisely the  $I_1$ – $I_4$  areas, each spectrum was

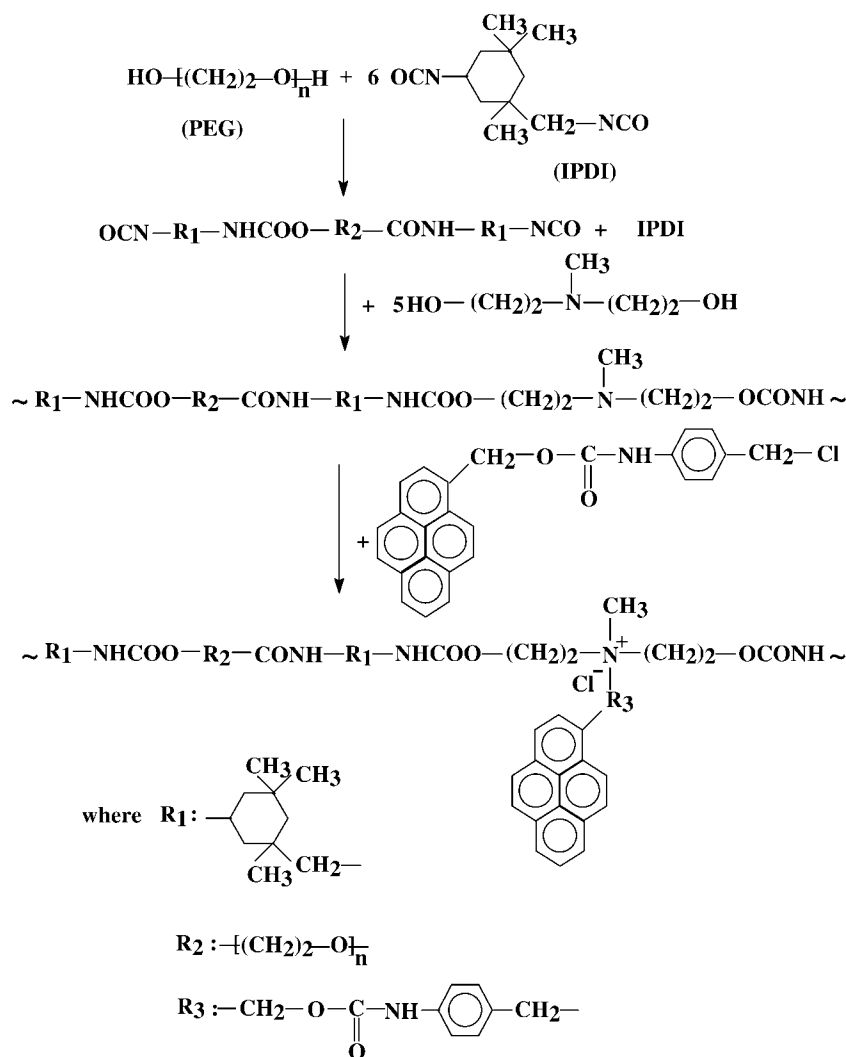
deconvolved into four Gaussian curves (Table 1). Thus, for Py-QA, a drastic decrease in the  $I_1/I_3$  ratio was observed as the excitation wavelength increased from 344 ( $I_1/I_3 = 0.96$ ) to 365 nm ( $I_1/I_3 = 0.26$ ). This effect could be explained by a distortion of the  $\pi$ -electron cloud around the pyrene molecule caused by the higher energy brought by a lower excitation wavelength. On the other hand, the ratio of the fluorescence intensities of the excimer ( $I_E$ ) and the monomer ( $I_M$ ) provides a direct method for the determination of the excimer efficiency. The ratio  $I_E/I_M$ , varying from 1.09 ( $\lambda_{\text{ex}} = 344$  nm) to 0.98 ( $\lambda_{\text{ex}} = 365$  nm), suggests that there is no dynamic exchange among the

**Table 1.** Parameters of the Gaussian Curves Resulting from Fluorescence Spectral Deconvolution

Sample	$\lambda_{\text{ex}}$ (nm)	Relative Peak Intensities ( $\lambda_F$ )					
		I <sup>a</sup>	II <sup>a</sup>	III <sup>a</sup>	IV <sup>b</sup>	V <sup>b</sup>	VI <sup>b</sup>
Py-QA (DMF)	344	6.143	13.950	6.399	20.019	—	—
	365	4.785	18.233	17.985	40.246	—	—
Py-PUC1 (DMF)	344	8.488	10.189	13.149	11.111	—	—
Py-PUC1 (THF)	344	5.51	13.20	10.60	40.98	—	—
Py-PUC1 (film)	344	7.05	10.32	11.47	27.05	—	—
Py-PUC2 (THF)	344	7.84	21.80	4.50	11.80	26.3	21.7
Py-PUC3 (THF)	344	3.87	10.99	2.27	11.75	25.77	21.63

<sup>a</sup> Monomer form.

<sup>b</sup> Excimer form.



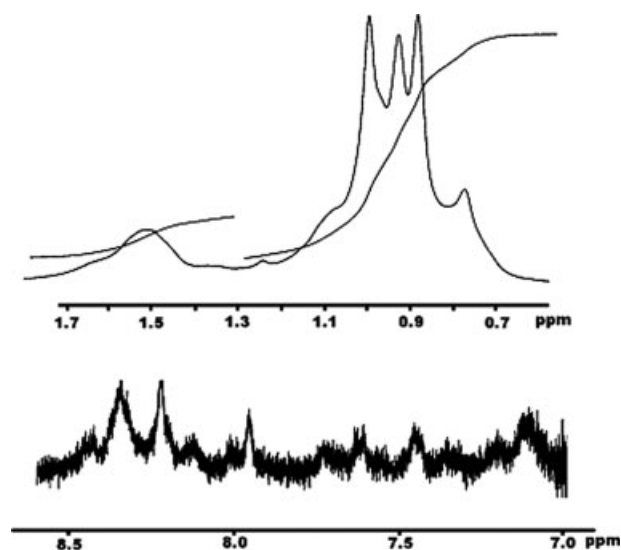
**Scheme 2.** Synthetic route to the pyrene polyurethane (Py-PUC1).

involved species during the emission and that the excitation wavelength does not have an important effect on the excimer-to-monomer ratio, the pyrene concentration and the excited-state lifetime probably being much more important.

### Characterization of the Polymers

A polyurethane precursor (PU-PR) with potential cationic functionality based on PEG ( $M_n = 2000$ ), IPDI, and NMDA (molar ratio = 1/6/5) was prepared in an attempt to develop hydrophilic PU ionomers possessing pyrene units on the ammonium quaternary structure. The pyrene rings of Py-QA were anchored by a partial quaternization of the aliphatic tertiary nitrogen atoms from the aforementioned polymer, and as result, two pyrene polyurethanes were synthe-

sized to compare their affinities toward photoluminescence (quaternization degree = 14.15% for Py-PUC1 and 0.65% for Py-PUC2). Scheme 2 shows the chemical structure of the pyrene polyurethane (Py-PUC1) used in our experiments. To afford a concentration of cationic groups about the same as that in Py-PUC1, it was important to realize an additional quaternization of Py-PUC2 by its subsequent reaction with benzyl chloride. The resulting polymers were differentiated by the amount of pyrene introduced into the polyurethane chain and appreciated by NMR data (Py-PUC1, 19.82 mmol of pyrene/100 g of polymer; Py-PUC2 and Py-PUC3, 1.14 mmol of pyrene/100 g of polymer). Furthermore, the concentration of ammonium quaternary groups obtained by the determination of the ionic chlorine content (Py-PUC1 and



**Figure 2.**  $^1\text{H}$  NMR spectra for the aliphatic protons from 1,3,3-trimethylcyclohexane (isophorone; upper graph) and for the aromatic protons of the pyrene derivative (lower graph) from Py-PUC2.

Py-PUC3) was close to the aforementioned values for both polymers. As shown in Figure 2 for the  $^1\text{H}$  NMR peaks assigned to the aromatic protons (7.8–8.33 ppm) belonging to the pyrene derivative and to the aliphatic protons (0.79–1.64 ppm) from 1,3,3-trimethylcyclohexane (isophorone) of the polymers (Py-PUC1 and Py-PUC2), there is very good agreement in the evolution of integrated areas. All the polymers were soluble in DMF and DMSO and, to a lesser extent, in THF. Although the polymers contained about 50 wt % hydrophilic segment of poly(ethylene oxide), they were insoluble in water at the ambient temperature because of the urethane hard component. Interestingly,

when water was slowly added to the polyurethane solution in THF (up to 1:1 v/v), it remained clear, but upon further dilution, the quality of the polymer solution decreased gradually so that it became turbid because of the emulsification process caused by a microphase separation between hydrophilic and hydrophobic segments of the polymeric chains. This is somewhat surprising and has led to the conclusion that because of the local solvation environment, a change of the polymer conformation may be possible.

As the physical properties of polyurethanes are primarily determined by the degree of phase separation between the soft and hard segments with the formation of microdomains, DSC analysis was carried out with the parent polyurethane. In this polymer, a single glass transition [glass-transition temperature ( $T_g$ ) =  $-12.5$  °C] assigned to the soft segment was observed. Comparing this value with that of pure poly(ethylene oxide) ( $T_g$  =  $-41$  °C), we have deduced that an increase in the degree of the hard-soft segment mixing in the PU matrix is possible,<sup>28</sup> and obviously the soft-phase transition is a sensitive indication of order within a PU.

### Fluorescence Spectra of Pyrene Polymers

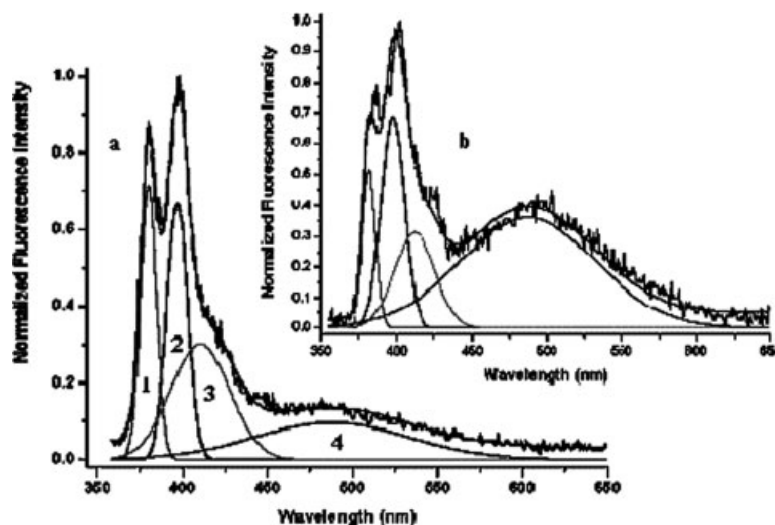
The Py-PUC series was studied in solvents of different quality (DMF and THF) and in a thin film for one of them for at least two reasons (Table 2). First, DMF is a good solvent for polyurethanes, including the pyrene moieties, and so a reduced number of ground-state pyrene associations could exist in this medium in which excimer formation occurs predominantly by diffusion. Second, the

**Table 2.** Principal Vibronic Bands and Intensity Ratios in Pyrene Fluorescence Spectra ( $I_1/I_3$  and  $I_F/I_M$ ) for the Pyrene Derivative and Ionic Polyurethanes

Sample	$\lambda_{\text{ex}}$ (nm)	Relative Peak Intensities ( $\lambda_F$ )						$I_1/I_3$	$I_F/I_M$
		I <sup>a</sup>	II <sup>a</sup>	III <sup>a</sup>	IV <sup>b</sup>	V <sup>b</sup>	VI <sup>b</sup>		
Py-QA (DMF)	344	384.35	488	420.5	487.25	—	—	0.959	1.095
	365	380.2	399.9	417.47	487.22	—	—	0.26	1.00
Py-PUC1 (DMF)	344	380.07	396.92	410.29	487.66	—	—	0.64	0.35
Py-PUC1 (THF)	344	382	397.5	412	487.5	—	—	0.52	1.398
Py-PUC1 (film)	344	380	397	410	487.5	—	—	0.614	0.937
Py-PUC2 (THF)	344	380	396.5	420	450.5	471.5	501	1.74	3.95
Py-PUC3 (THF)	344	380	396.5	420	450.5	471.5	501	1.40	3.11

<sup>a</sup> Monomer form.

<sup>b</sup> Excimer form.

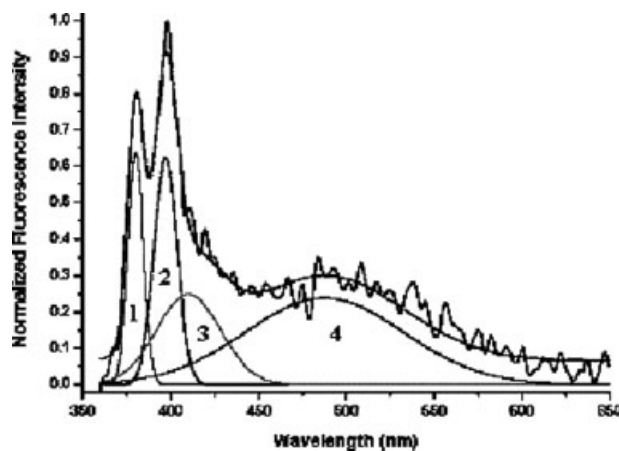


**Figure 3.** Deconvolution results of the fluorescence spectra in (a) DMF and (b) THF for the polymer Py-PUC1 at  $\lambda_{\text{exc}} = 344$  nm: (1–3) monomer fluorescence and (4) excimer fluorescence.

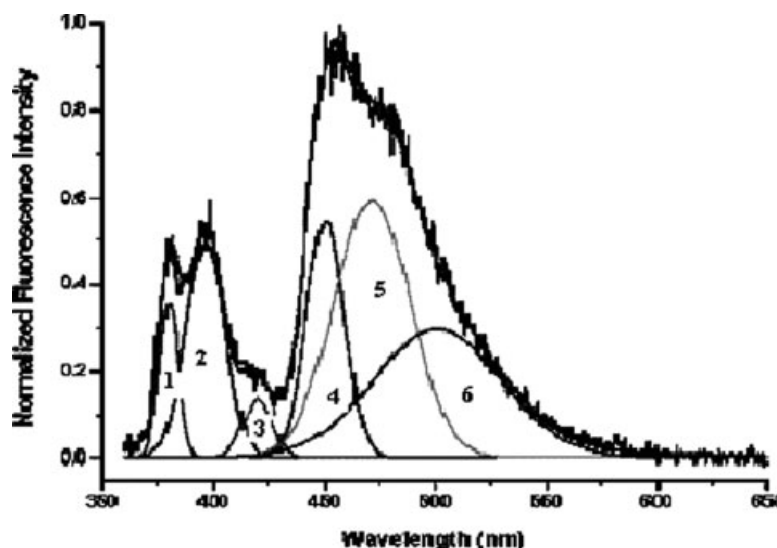
THF quality is not so good for polymers, but it is good for pyrene, and in a such solvent, just a few pyrene–pyrene interactions between the pyrene rings seem to be favored.<sup>12</sup> Consequently, the polymers are expected to adopt a more collapsed conformation in THF than in DMF. Table 2 summarizes the relative positions of the principal vibronic bands in the pyrene–polyurethane fluorescence together with tentative assignments.

Figure 3(a,b) illustrates the fluorescence spectra for Py-PUC1 in DMF and THF. The spectra are identical to those of the pyrene derivative, except for the maximum of the blue monomer fluorescence ( $I_1$  and  $I_2$ ) and the third peak ( $I_3$ ), which are shifted in the polymer by about 2–4 nm and by 10 nm, respectively. In such a case, the vibrational fine structure undergoes changes with the transfer of pyrene from a polar environment to a nonpolar one, suppressing thus the allowed and forbidden vibrations including the 0–0 band. The resultant changes can be described with the  $I_1/I_3$  ratio, that is, the intensities of the first and third bands in the pyrene fluorescence spectrum. At a first approximation, the observed shifts can be attributed to the formation of hydrophobic associates, which increase with decreasing solvent polarity. According to the ratio of the intensity of the green excimer fluorescence ( $I_E$ ) from 487.5 nm to the monomer fluorescence intensity ( $I_M$ ) from 380, 397, and 410 nm, the emission of Py-PUC1 is characterized by an increased excimer emission (excited dimer). This is a result of

the high concentration of pyrene located on the polymeric chain when the probability of two pyrene molecules meeting increases. Therefore, in a low-polarity solvent such as THF ( $I_E/I_M = 1.39$ ), the aggregation of cationic groups containing hydrophobic pyrene in their structure leads to the formation of hydrophobic aggregates with a hydrophilic interior, whereas in DMF ( $I_E/I_M = 0.35$ ), single polyions coexist as well as free aggregates with polyions and counterions, manipulated tightly by electrostatic forces. The quantum fluorescent yield of fluorescence ( $\phi$ ) of Py-PUC1 and



**Figure 4.** Deconvolution results of the emission spectra of polymeric films based on Py-PUC1 at  $\lambda_{\text{exc}} = 344$  nm: (1–3) monomer fluorescence and (4) excimer fluorescence.



**Figure 5.** Plot of the deconvolution results of (1–3) monomer fluorescence and (4–6) excimer fluorescence for Py-PUC3 in THF at  $\lambda_{\text{exc}} = 344$  nm.

Py-PUC2 ( $\phi = 0.2$ ) in DMF solutions is smaller than that determined for the pyrene derivative ( $\phi = 0.34$ ) in the same solvent. On the other hand, the ratio of the first vibronic band to the third vibronic band ( $I_1/I_3$ ) in the fluorescence spectrum of pyrene reflects the polarity in local media in which the fluorophore exists; a minor solvent-sensitive variation from 0.52 (THF) to 0.64 (DMF) is not suggestive enough to discuss and differentiate environmental effects on the aforementioned pyrene-polyurethane fluorescence.

As we can see in the fluorescence spectrum of the polymeric film (Fig. 4), in agreement with the ratio found in the film state ( $I_1/I_3 = 0.61$ ), and in comparison with the value obtained for an unsubstituted pyrene in hexane ( $I_1/I_3 = 0.6$ ),<sup>27</sup> we can appreciate that the environmental polarity in the vicinity of pyrene rings is hydrophobic. Examining the  $I_E/I_M$  ratio for the polymeric film ( $I_E/I_M = 0.93$ ), we note that the latter value could validate the aforementioned prediction. This is fitting as a measure of the hydrophobic character of the pyrene residues and its ability to form a larger amount of excimers in THF and in the film state with respect to the monomer emission.

Monitoring then the process of excimer formation as the concentration of pyrene used in the preparation of the polymers decreases, we can observe a marked increase in the  $I_1/I_3$  ratio for Py-PUC2 ( $I_1/I_3 = 2.36$ ) and Py-PUC3 ( $I_1/I_3 = 1.7$ ) in THF. An example is given in Figure 5

for Py-PUC3. This trend suggests rather a hydrophilic environment for pyrene from both polymers that, contravening the hydrophobic probe, is not yet well understood. Such an effect is displayed by the spectroscopy of the fluorescent pyrene in Nafion neutralized by  $\text{Na}^+$  and swollen in water ( $I_1/I_3 = 1.47$ ).<sup>13</sup> A careful examination of the fluorescence data (Table 2) shows that the emission of pyrene polymers 2 and 3 is blue ( $I_1$ ) and redshifted ( $I_3$ ) by about 2 and 8 nm, respectively, but in every case, the excimer emission (450.5, 471.5, and 501.0 nm) is better structured than Py-PUC1. Under basic conditions, normally the  $I_E/I_M$  ratio for a polymer with a small amount of pyrene should be lower because a larger number of pyrene molecules are isolated and there is no interaction to form excimers.<sup>8</sup> This problem was not confirmed in our case, in which the spectral analysis of the Py-PUC2 ( $I_E/I_M = 3.95$ ) and Py-PUC3 ( $I_E/I_M = 3.11$ ) solutions indicated that the recorded values were significantly higher than that obtained for Py-PUC1. As both polymers had about the same quantity of pyrene anchored onto the polyurethane backbone (1.14 mmol), it is reasonable to believe that the microenvironment polarity in the vicinity of pyrene rings led to a diminution in the excimer emission in Py-PUC3, for which the contribution of the cationic groups even at the lowest concentration was suspected. This seems to be consistent with a change in the conformation of the polyurethane chain from a coil form in

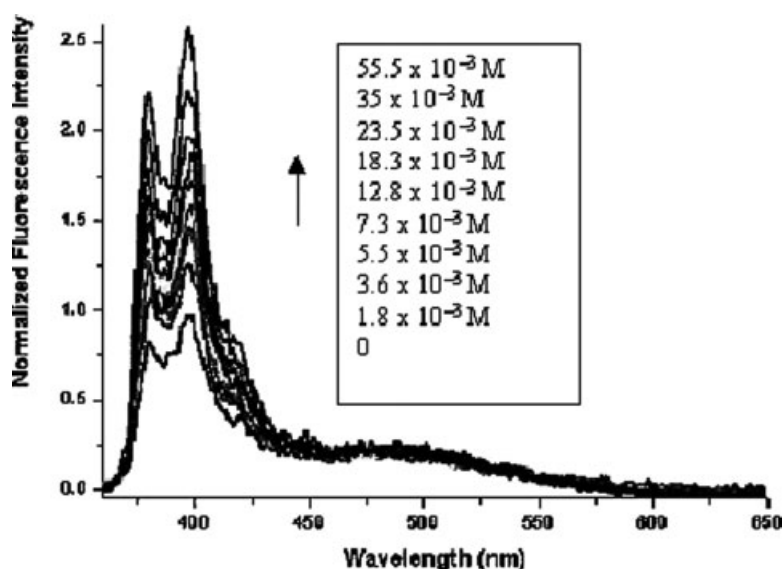


Py-PUC2 to an extended conformation in Py-PUC3, induced in the latter by the electrostatic repulsion between the positive charges into the polymer. Such a conformation is known to prevent the formation of an excimer structure by pyrene in THF, and consequently, a weaker excimer emission can be detected in Py-PUC3. When Py-PUC1 at 365 nm and Py-PUC2 and Py-PUC3 at 397 nm were excited, only an excimer form was obtained. However, the level of association between the pendant pyrene rings could be the result of the combinative effect of hydrophobic/electrostatic forces, and so the ratio of monomer-to-excimer emission intensities is indeed a suggestive indicator of the structure of the ionic polyurethanes in solution. Clearly, the pyrene content plays a key role in the fluorescence profiles of the polymers. The assessment of the  $I_E/I_M$  parameter in polymer solutions with about the same ionomer concentration but with different pyrene contents (Py-PUC3 and Py-PUC1) has shown that a certain model for a realistic description of the system is a more difficult task.

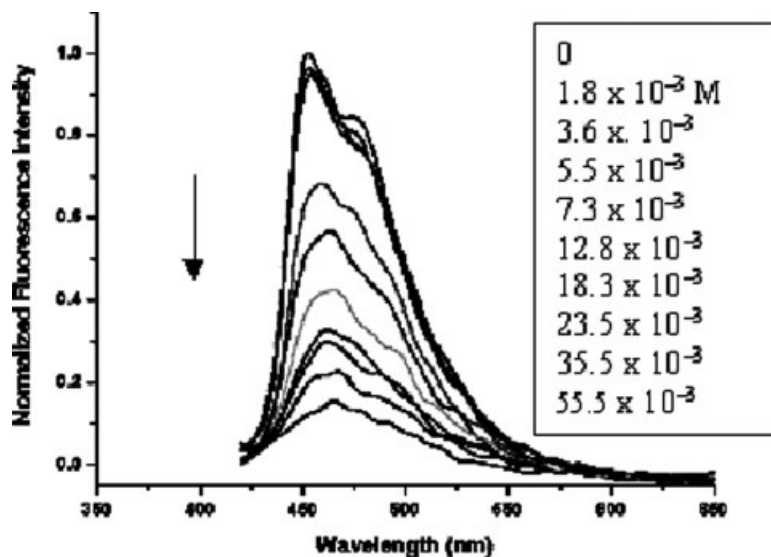
On the other hand, the fluorescence of the cationic polyurethane containing more pyrene (Py-PUC1; 19.82 mmol) increased with increasing pure water content in the mixed solvent (THF/H<sub>2</sub>O). Figure 6 demonstrates that less excimer was formed in THF/H<sub>2</sub>O (Py-PUC1) than in the single solvent, as was previously shown in the spectrum of one polyelectrolyte hydrophobically modified with pyrene.<sup>12</sup> Although water is a poor

solvent for pyrene and usually leads to pyrene-pyrene associations, its presence in a nonpolar medium (THF) perturbs the behavior of the amphiphilic polyurethane, in which the repulsive electrostatic forces associated with the cationic charges are counteracted by pyrene-pyrene attractive hydrophobic forces. Besides the polymer structure, which affects aggregation because pyrene itself is a part of the ionic hard segment from the polyurethane chain, the aggregation and the aggregate size are determined by a subtle balance between the attractive forces and the steric repulsion ones.

In analogy with other block copolymers,<sup>29</sup> one could easily imagine that the formation of various morphological aggregates with a binary solvent mixture of THF and water in a polymer solution typically occurs because water is a selective solvent for associating amphiphilic polymeric chains. Therefore, when water is added to a Py-PUC1 solution, the formation of micelle-like structures with a hydrophobic core surrounded by a corona of poly(ethylene oxide) with a molecular weight of 2000 and ammonium charges is promoted, and this variable seems to control the morphology of the resulting micelles and, implicitly, the emission intensities. Additionally, the nature of the solvent mixture exerts a remarkable influence on the morphology of the micelles, often causing a change in the internal structure.<sup>30</sup> As the amount of water increases, dispersed domains in a continuous hydrophilic



**Figure 6.** Water effect on the fluorescence spectrum of Py-PUC1 in THF at  $\lambda_{exc} = 344$  nm.



**Figure 7.** Fluorescence decay profiles for Py-PUC2 in THF with water at  $\lambda_{\text{exc}} = 397$  nm.

phase are formed in pyrene polyurethanes, but unfortunately, the interpretation of the polymer/mixed-solvent interactions and the role of the ionic content in determining the solution structure, the association dynamics, and the character of the micellar core is not well argued yet.

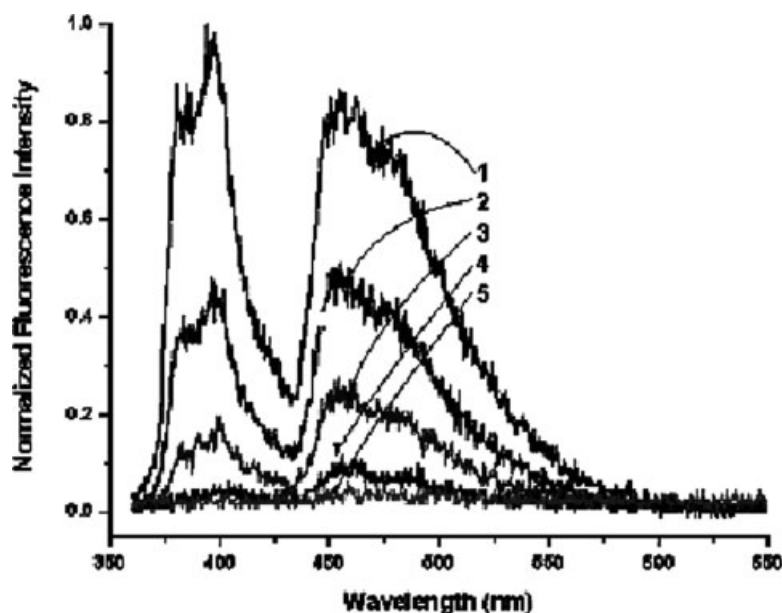
By contrast, at a low concentration of pyrene (1.14 mmol), the addition of water to Py-PUC2 and Py-PUC3 solutions (not shown) reduces monomer and excimer fluorescence. The reduction of the fluorescence peak intensity suggests that the number of pyrene molecules available for aggregation inside the hard domain is relatively low, thus generating smaller aggregates; this is consistent with the intermolecular association of pyrene within the micelle core. At first glance, water is a quencher of pyrene fluorescence for these polymers ( $\lambda_{\text{exc}} = 344$  nm) in a region of increasing polarity, in which the quenching of the excimer band (ca. 60%) is more efficient than that of the monomer one (15%). Similar data have also been obtained for polymers excited at 397 nm, as can be observed for Py-PUC2 (Fig. 7), but these aspects will be discussed further in detail because no other methods were readily accessible to us in the course of this work.

#### Fluorescence Quenching Experiment

One of the well-studied quenchers of pyrene fluorescence is nitromethane, which has a high

affinity for hydrophobic environments and whose quenching efficiency is essentially diffusion-controlled by an electron-transfer mechanism. The quenching of the excited pyrene by nitrobenzene as a nonionic quencher suitable for organic solvents could provide a means of controlling the pyrene lifetime. For example, the effect of the quencher concentration on the fluorescence decay of a pyrene polyurethane (Py-PUC2) is shown in Figure 8. Indeed, the fluorescence of Py-PUC2 in THF is quenched by the addition of nitrobenzene to the polymeric solution; the intensity of both the excimer and monomer emissions decreases as the concentration of nitrobenzene increases from  $4.8 \times 10^{-6}$  to  $9.6 \times 10^{-5}$  M. If the excimer fluorescence decays at about 65% with  $24.3 \times 10^{-6}$  M nitrobenzene, the quenching of the monomer one at the same concentration of the quencher is around 85%. For a higher concentration of nitrobenzene ( $48.6 \times 10^{-6}$  M), a complete quenching of the monomer fluorescence has been observed.

Moreover, an analysis of the fluorescence decay in Py-PUC2 and Py-PUC3 has indicated that the  $I_1/I_3$  ratio is not affected by the addition of the quencher to the polymeric solution, and this confirms that excimer formation by a diffusion process is preferentially influenced. Returning to a Py-PUC1 solution, we detected a rapid quenching of the excimer fluorescence after the addition of  $24.3 \times 10^{-6}$  M nitrobenzene, whereas



**Figure 8.** Fluorescence spectra of Py-PUC2 in THF in the absence and presence of nitrobenzene at various concentrations: (1) 0, (2)  $9.7 \times 10^{-6}$ , (3)  $24.3 \times 10^{-6}$ , (4)  $38.8 \times 10^{-6}$ , and (5)  $48.6 \times 10^{-6}$  M (5).

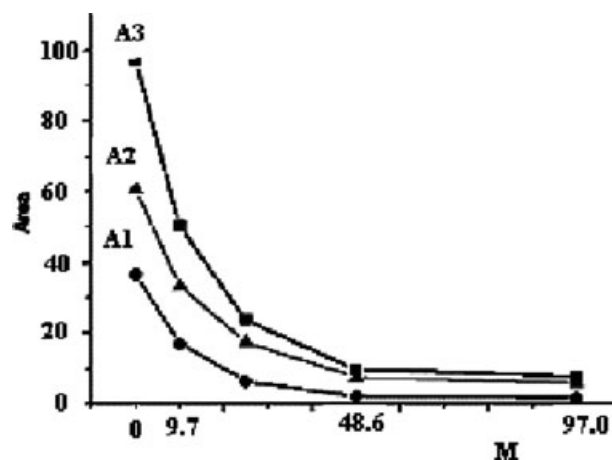
this concentration of the quencher affected only 80% of the monomer fluorescence.

However, despite small differences in the polymers considered in this study, fluorescence quenching in solution normally follows Stern–Volmer kinetics,<sup>9</sup> at least for the polymers carrying a few mole percent of pyrene (Py-PUC2 and Py-PUC3). From the data given in Figure 9, we can obtain a Stern–Volmer plot of the quenching of pyrene monomer fluorescence that is nearly a perfectly straight line for a concentration of the quencher lower than  $24.3 \times 10^{-6}$  M (not shown here). At higher concentrations of nitrobenzene, the slope of the plot increases, reaching a curvature. In summary, pyrene fluorescence quenching by nitrobenzene exhibits a kinetic behavior more appropriate with an apparent Stern–Volmer diffusion–quenching model that probably occurs via two different mechanisms. To explain these results and to realize the advantages of the polymers for possible sensor applications, more information about the quenching mechanism and an understanding of the nature of the solvation environment of the discussed polymers and how it is affected are essential.

## CONCLUSIONS

A series of hydrophilic polyurethanes carrying pyrene pendants incorporated into polymers via

a quaternization reaction with a pyrene derivative, Py-QA, were synthesized. In addition to the polymers reported here (Py-PUC1, 19.82 mmol of fluorophore/100 g of polymer; Py-PUC2, 1.14 mmol of fluorophore/100 g of polymer), a third polyurethane with a low pyrene content (Py-PUC3, 1.14 mmol of fluorophore/100 g of polymer) and with a concentration of quaternary



**Figure 9.** Relationship between (A3) the total area of the monomer and excimer fluorescence, (A2) the area of monomer fluorescence for 380, 396.5, and 420 nm, and (A1) the area of the excimer fluorescence for 450.5, 471.5, and 501 nm and quenching for Py-PUC2 at different concentrations (0, 9.7, 24.3, 48.6, and  $97.0 \times 10^{-6}$  M) of nitrobenzene.

ammonium groups like that in Py-PUC1 was also prepared. The pyrene derivative and all the polyurethanes were characterized with spectral techniques ( $^1\text{H}$  NMR, IR, UV-vis, and fluorescence spectroscopy), thermal methods (DSC), and gel permeation chromatography/viscosity measurements for the precursor. Related to the pyrene derivative, the synthesized polymers had fluorescence properties, and their fluorescence decay acquired in THF and DMF solutions indicated the presence of a certain level of association between the pyrene moieties attached to the ionic groups. The existence of the aggregates or dimerized probe in the ground state of the molecule was indicated by the high excimer-to-monomer intensity ratio. The effects of the solvent, pyrene content, and concentration of ionic groups could be explained in terms of hydrophobic and electrostatic forces. Depending on the pyrene content, the addition of water to the THF polymeric solutions sustained the intermolecular association of the pyrene rings within the micelle core with the effect of increasing (Py-PUC1) or decreasing (Py-PUC2 and Py-PUC3) fluorescence. The results of the fluorescence quenching experiments reported in terms of the Stern-Volmer model corresponded to linear Stern-Volmer plots for the quenching of the pyrene excimer and monomer emissions in Py-PUC2 and Py-PUC3 solutions (THF) arising from an effective interaction with the quencher ( $<24.3 \times 10^{-6}$  M).

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