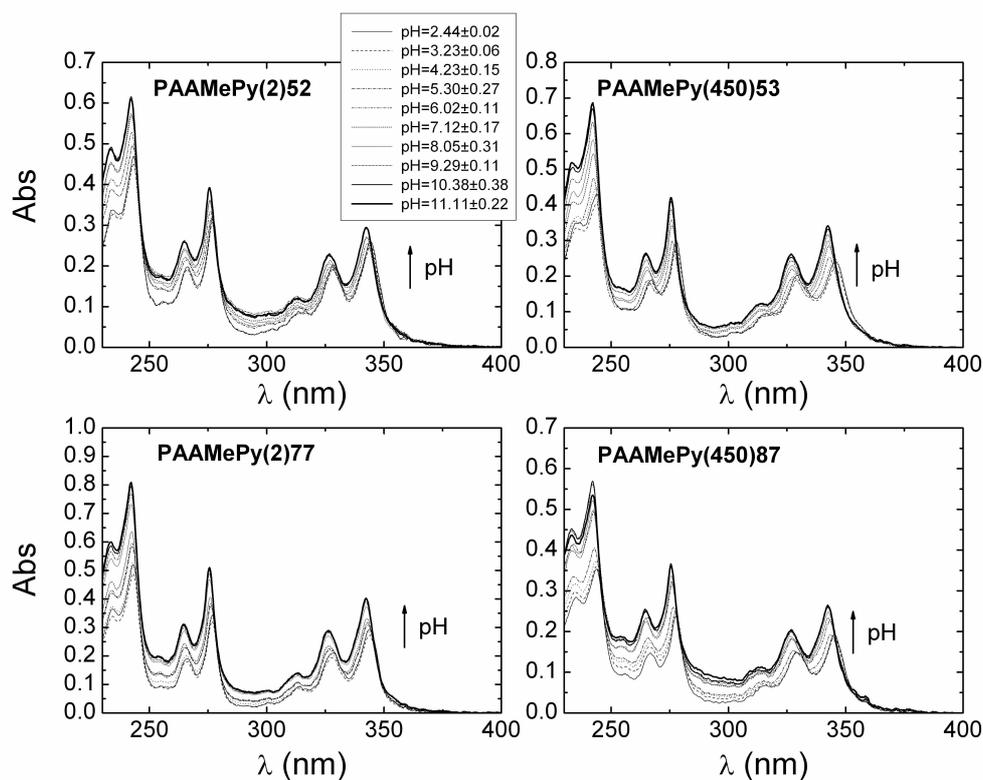


## Supplementary Information

### *Absorption spectra dependence with pH and potentiometric titrations*

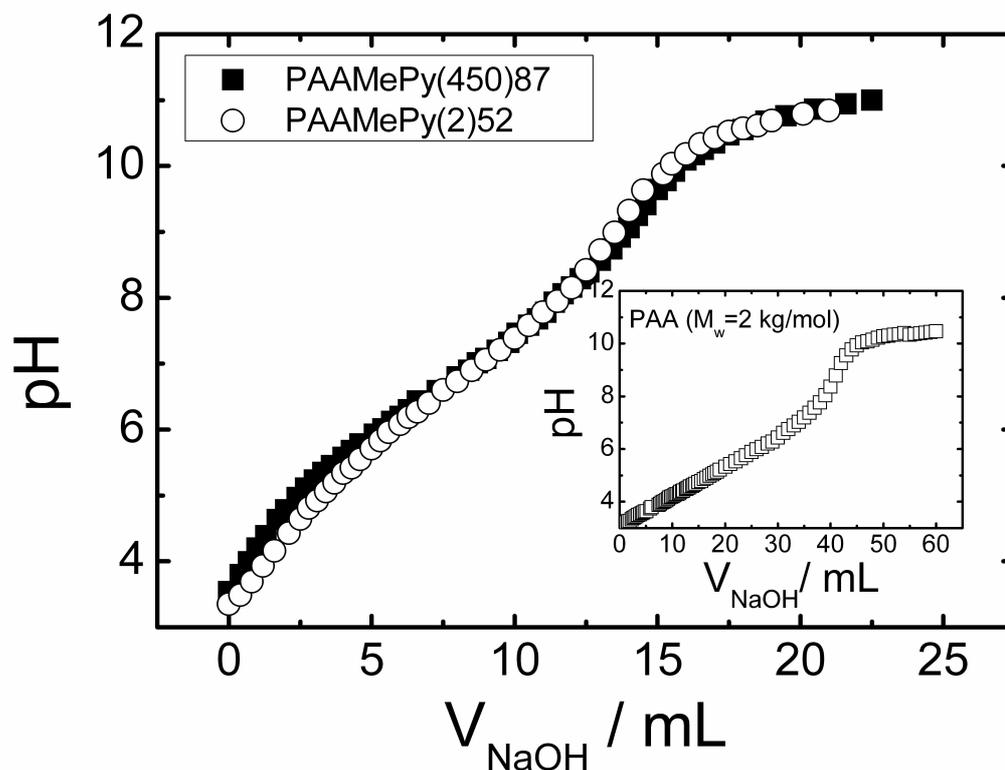
Figure S1 displays the dependence of the absorption spectra of the PAAMePy polymers with the pH, which clearly shows a shift in the wavelength maxima ( $\lambda_{max}$ ) and a variation of the  $P_A$  parameter. The variation of these two parameters with pH is presented in Figure 1.



**Figure S1**-Absorption spectra for the PAAMePy(2) (left hand panels) and PAAMePy(450) (right hand panels) polymers as a function of the pH.

The potentiometric titrations of the short and long size PAA pyrene tagged polymers together with the titration of an untagged PAA with low  $M_w$  (2 kg/mol) are shown in Figure S2. Comparison of the titration curves shows that between pH 3 and 7 the titration curves of the two pyrene labeled polymers are different from that of the untagged polymer, indicating that the hydrophobic probe influences the polymer degree of deionization. The potentiometric titration curves in Figure S2 are clearly different from the acrylic acid-base titration curve due to the coexistence of different deionization degrees within the polymer which leads to a dependence of the pH with the dissociation degree. Moreover this dependence means that the  $pK_a$  values that can be estimated from

the absorption spectra should be regarded as “local”  $pK_a$  values, i.e., due to the specific environment felt by the probe.



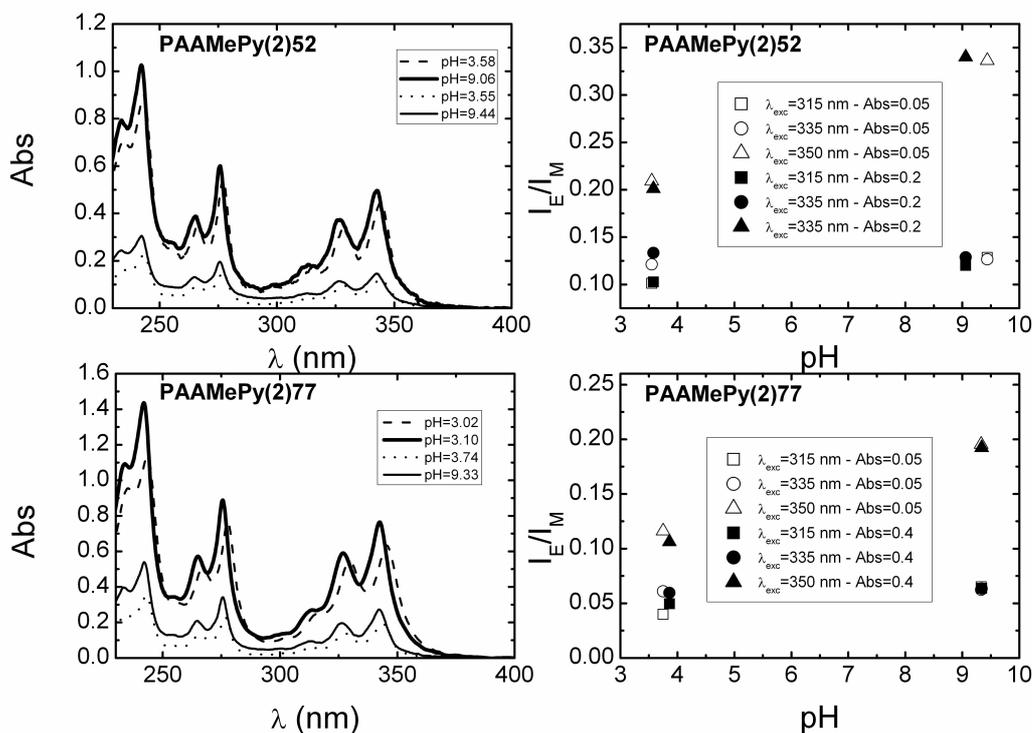
**Figure S2**-Titration curves for a small [PAAMePy(2)52] and long [PAAMePy(450)87]  $M_w$  PAA pyrene labeled together with the titration curve (inset) for the low  $M_w$  (2kg/mol) unlabeled polymer.

The pH of PAA strongly depends on its degree of ionization.<sup>1</sup> Consequently this has implications in the apparent  $pK_a$  values (as seen from the inflexion in the  $P_A$  and  $\lambda_{max}$  vs. pH plots). For example for the PAA polymers for a dissociation degree  $\alpha=0.316$  one obtains a pH= 5.5, whereas for  $\alpha\approx 0.9$ , i.e., 90% of the carboxylate groups are ionized the pH is 8.08; these values were obtained from equation  $pH = 6.17 - 2 \log\left(\frac{1-a}{a}\right)$  taken from ref.<sup>1</sup>.

### *Concentration dependence*

Figure S3 shows the absorption spectra of the PAAMePy(2) polymers obtained with two different concentrations (the OD @ the excitation wavelengths vary from a ratio of  $\approx 4$ ) and at acidic (pH $\approx 3.5$ ) and alkaline (pH $\approx 9.3$ ) media together with the resultant  $I_E/I_M$ . This  $I_E/I_M$  displays, within the experimental error, the same values, independent of the solution concentration of the polymer. This ratio is also shown at three different

excitation wavelengths. The data reveal that we are in the presence of pure intramolecular interactions (see text for more details).

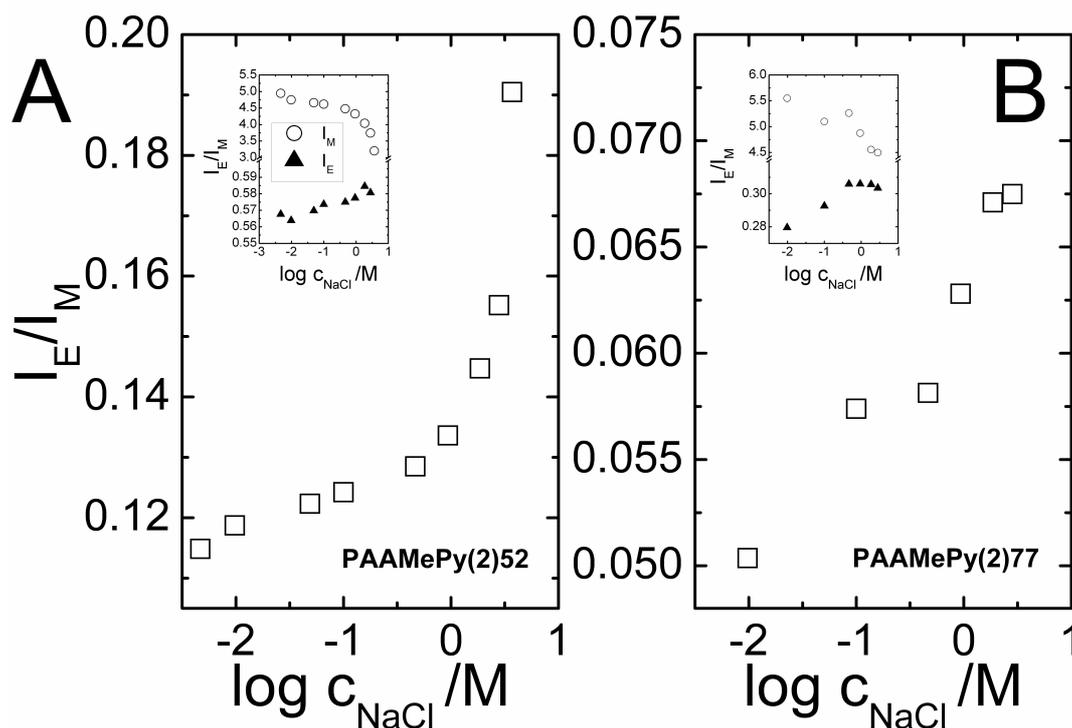


**Figure S3-** Absorption (left hand panels) spectra for the two PAAMePy(2) polymers obtained with two different concentrations and @ acidic (pH $\approx$ 3.5) and alkaline (pH $\approx$  9.3) media and  $I_E/I_M$  ratio (right hand panels) for this same solutions obtained with three different excitation wavelengths.

#### *Effect of Salt (NaCl) addition*

The effect of salt addition (NaCl) on water solutions of the short polymers (PAAMePy(2)) was also investigated. For the PAAMePy(2) at pH=10 (meaning that  $\alpha=0.988$ , i.e., ca 99 % of the  $-\text{COOH}$  groups are deionised), the  $I_E/I_M$  plots vs. the  $\log_{10}[\text{NaCl}]$ , with  $[\text{NaCl}]$  ranging from  $1 \times 10^{-3}$  M to 4 M (close to the solubility limit of NaCl in water), are shown in Figure S4. The addition of salt induces a gradual increment of the  $I_E/I_M$  ratio. If the individual  $I_E$  and  $I_M$  intensities are observed (see insets in Figure S4) it can be seen that the  $I_E$  values slightly increase whereas the  $I_M$  values strongly decrease with the addition of salt. The observation suggests that the increase in the  $I_E/I_M$  for high salt concentrations results from the contraction of the polymer, as elsewhere suggested for naphthalene-labeled PAAs,<sup>2</sup> due to the lowering of the entropy of the counterion distribution or because of the reduction on the strength of the electrostatic repulsion between the ionized carboxylic groups due to the sodium ions. However this decrease of the  $I_M$  values with increased NaCl concentration can be

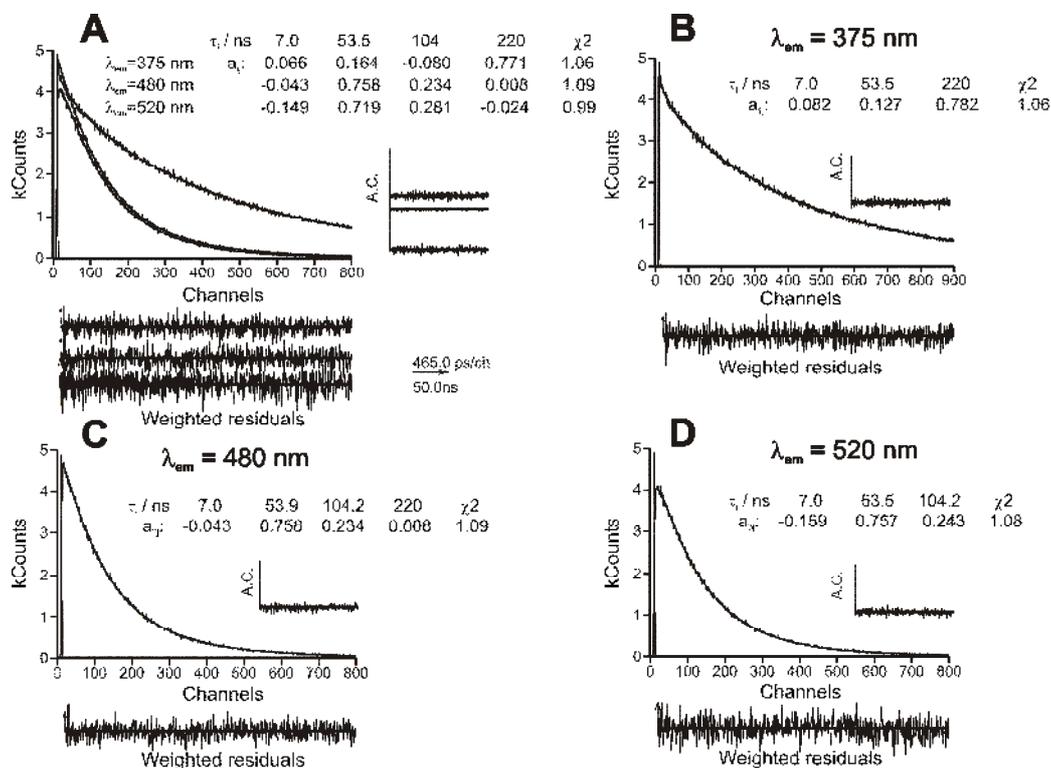
ate least partially appointed to the quenching by the chlorine ion. In fact, since the monomer lifetime is greater than that of the excimer, the quenching by the  $\text{Cl}^-$  would affect more the  $I_M$  intensity than that of  $I_E$  thus giving rise to the observed rise of the  $I_E/I_M$  ratio.



**Figure S4** – Variation of the  $I_E/I_M$  ratio as a function the NaCl concentration (in a logarithmic scale) for (A) PAAMePy(2)52 and (B) PAAMePy(2)77 polymers, at pH=10. Shown as insets are the dependence of the monomer and excimer intensities on the NaCl concentration.

#### *Decays with Global and Independent Analysis- In Water*

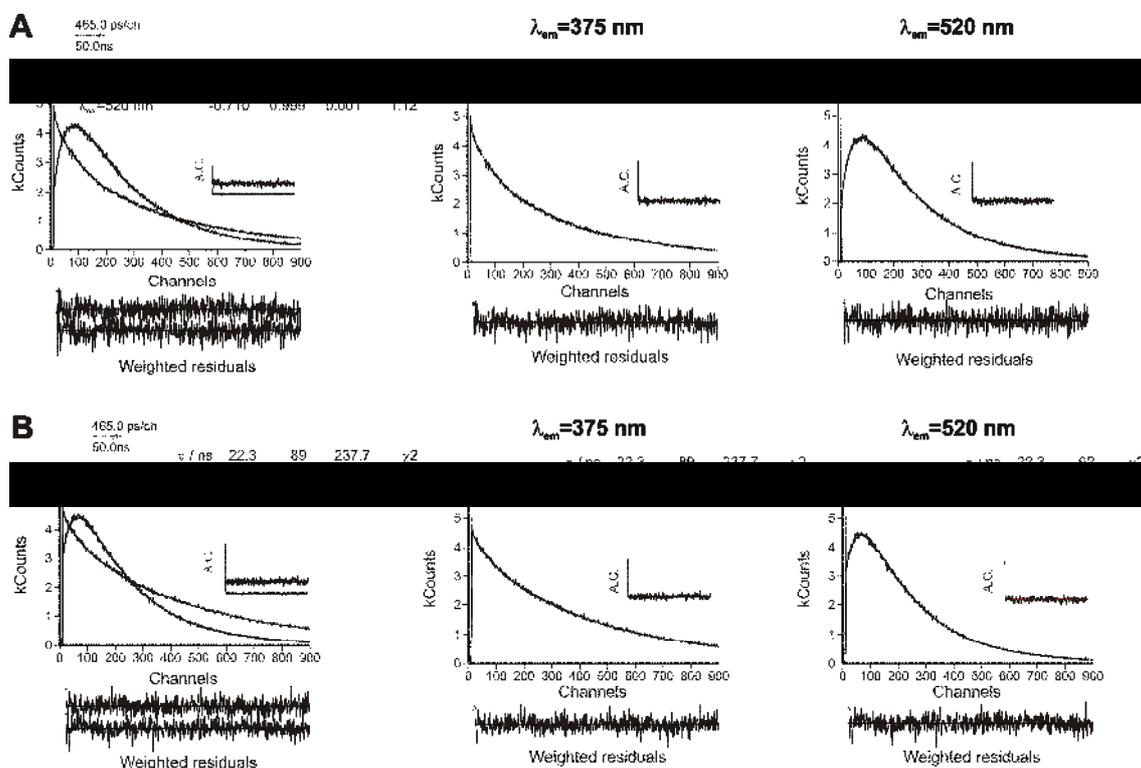
Figure S5 shows the global and independent analysis of the decays. As discussed, the independent analysis of the 480 nm decay requires a sum of four exponentials as well as the global analysis does. As shown in the manuscript, a comparison between the decays with fits resulting from an inferior number of exponentials is shown in SI attesting the need of three exponentials at the emission wavelengths of 375 and 520 nm and of four exponentials at 480 nm to properly fit the decays. This is more clearly observed with the independent analysis shown in Figure S5.



**Figure S5** - Fluorescence decays of PAAMePy(2)52 in water (pH= 4.62, T=293 K), at three emission wavelengths: A) global analysis and independent analysis of the decays at B) 375 nm C) 480 nm and D) 520 nm. The instrument profile curve, weighted residuals and autocorrelation (A.C.) functions are also shown. The negative preexponential values of the longest times in the global analysis result are artifacts resulting from this kind of analysis, i.e., the components do not exist, as seen in the individual analysis.

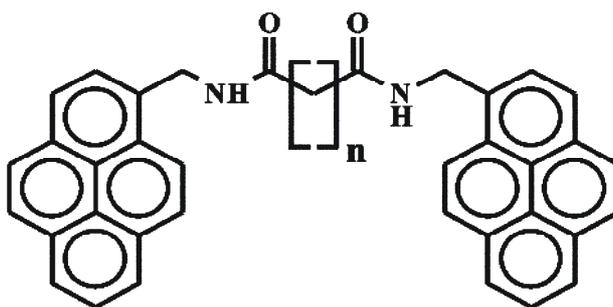
### *Decays with Global and Independent Analysis- In Good Solvents*

Note that in good solvents there is no need of a 4-exponential adjustment and thus the global (Figure 7) and independent analysis (Figure S6) of the decays give rise to essentially the same results.



**Figure S6-** Decays fitted with global and individual analysis of the fluorescence decays for (A) PAAMePy(450)87 and (B) PAAMePy(2)77 obtained in methanol at  $T=293\text{ K}$  with excitation at  $339\text{ nm}$  and emission at  $375$  and  $520\text{ nm}$ . The instrument profile curve is also shown. For a better judgment of the quality of the fits shown as insets are the weighted residuals and the autocorrelation (A.C.) functions.

In Figure S7 we present the emission spectra of the compound in scheme S1. This can be seen as a first example of a model compound for PAAMePy polymers aiming to obtain correlate the excimer formation rate constants in these compounds with the PAAMePy polymers. As can be seen from the structure of the compound, an effective number of 16 atoms ( $14\text{C} + 2\text{N}$ ) exists between the two pyrene units.

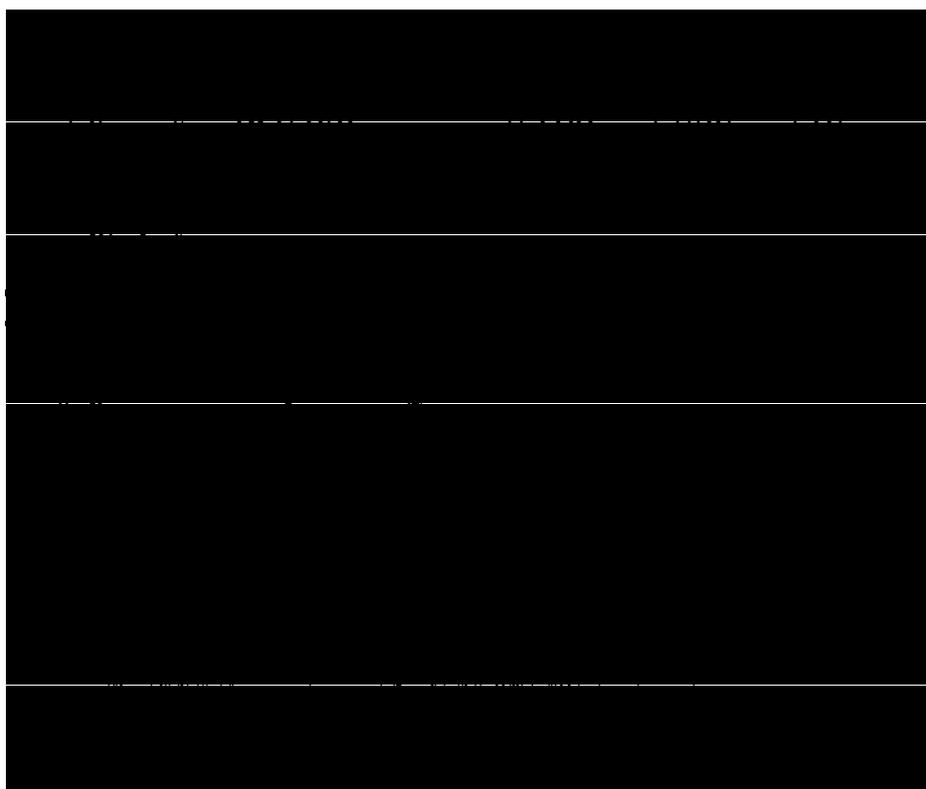


**Scheme S1:** acronym for the structure in  $\text{PyCH}_2\text{NHCO}(\text{CH}_2)_n\text{CONH}(\text{CH}_2)\text{Py}$ , with  $n=10$ .



**Figure S7-** Fluorescence emission of compound in scheme S1 in dioxane at T= 293 K and  $\lambda_{exc}$ = 339 nm.

A fluorescent decay of  $\text{PyCH}_2\text{NHCO}(\text{CH}_2)_n\text{CONH}(\text{CH}_2)\text{Py}$  in dioxane is shown below in Figure S8 together with the decay times and pre-exponential factors. Note that the sum  $a_{22}+a_{21}$  is different from zero thus denoting the presence of GSD. A detailed study on this and other related compounds is under progress and will be presented elsewhere.



**Figure S8-** Fluorescent decays collected at 375 nm and 520 nm for the model compounds in scheme S1. An additional longer component of  $\tau= 167.5$  ns exists @ the 375 nm emission wavelength but is absent at 520 nm. This contamination results from the starting material  $\text{PyCH}_2\text{NH}_2$  but with our analysis program this lifetime can be fixed and thus does not influence the obtained results.

## References

- 1 A. Katchalsky and P. Spitnik, *Journal of Polymer Science*, 1947, **2**, 432-446.
- 2 K. Schillén, D. F. Anghel, M. D. Miguel and B. Lindman, *Langmuir*, 2000, **16**, 10528-10539.