

DOI: 10.1002/((please add manuscript number))

Article type: Communication**Tuning the exciton diffusion coefficient of polyfluorene based semiconducting polymers***Muhammad T. Sajjad¹, Alexander J. Ward¹, Arvydas Ruseckas¹, Ashu K. Bansal¹, Sybille Allard², Ullrich Scherf² and Ifor D. W. Samuel^{1*}*¹Organic Semiconductor Centre, SUPA, School of Physics & Astronomy, North Haugh, St Andrews, KY16 9SS, United Kingdom²Chemistry Department and Institute for Polymer Technology, Wuppertal University, Gauss-Str. 20, D- 42119 Wuppertal, GermanyE-mail: ids@st-andrews.ac.uk**Keywords:** exciton diffusion, fluorescence, light emitting polymers, OLEDs, photoysics

Abstract: Exciton diffusion plays an important role in functional materials used in organic optoelectronic devices, such as solar cells, organic light emitting diodes (OLEDs) and lasers. Here we explore how exciton diffusion can be controlled in highly fluorescent blue-emitting polyfluorene materials by changing the length and type of side chains. We find that the exciton diffusion coefficient (D) decreases from $1.2 \times 10^{-3} \text{ cm}^2/\text{s}$ to $0.2 \times 10^{-3} \text{ cm}^2/\text{s}$ when the side chain length is increased from 8 to 12 carbon atoms. Other changes to the side chains led to enhancement of D up to $1.6 \times 10^{-3} \text{ cm}^2/\text{s}$. Our results show that small adjustments to the molecular structure can be helpful for the future development of high-brightness organic light emitting devices.

Exciton diffusion is very important for organic optoelectronic devices including organic photovoltaics (OPVs), organic light emitting devices (OLEDs), organic lasers and sensors. In OPVs, it determines the distance excitons can travel to an interface between donor and acceptor and contribute photocurrent.^[1, 2] In OLEDs and organic lasers, it can lead to either exciton-exciton annihilation or diffusion of excitons to non-radiative quenching sites and hence loss of efficiency^[3-6]. Conjugated polymer sensors often work by diffusion of excitons to an analyte (e.g. explosive molecule) that quenches fluorescence.^[7, 8] Hence larger exciton diffusion length

(L_D) is needed for OPVs and sensors, whereas, short L_D is desirable for LEDs and lasers. Therefore having control over the exciton diffusion is necessary for future optoelectronic devices

Most studies of exciton diffusion have been performed on organic semiconductors used in photovoltaics and a range of different values of the diffusion coefficient (D) have been reported in the literature. In these studies, a significant amount of work has been done to enhance the exciton diffusion using different processing strategies including annealing (both thermal and solvent vapour annealing)^[9-12] and dilution of molecules in an inert host^[13]. Compared to the effort put into enhancing exciton diffusion for photovoltaics, not much work has been done on tuning (reducing) the exciton diffusion for light emitting devices except for reports where exciton diffusion is controlled by confining the excitons using additional layers^[14, 15]. These methods of controlling the exciton diffusion are complicated and difficult to implement in solution processable light emitting devices. A simpler approach to control exciton diffusion is through a small modification of chemical structure. There are a few reports where exciton diffusion has been investigated as a function of the chemical structure.^[1, 16-18], but these have concentrated on photovoltaic rather than light-emitting materials.

Previously we have shown that exciton diffusion can be controlled in conjugated polymers^[19] and small molecules through simple modification of side chains.^[10] Here we investigated the influence of side chain on exciton diffusion in several polyfluorene derivatives. The polyfluorenes are prototypical blue-emitting polymers, extensively used for LEDs, lasers, and sensors yet the exciton diffusion in these materials is little studied, particularly with regard to the effect of molecular structure. We measured exciton diffusion using volume quenching method by dispersing different concentrations of fullerene quencher molecules in polyfluorenes. We found that exciton diffusion was the dominant process at lower concentrations of quencher, whereas direct FRET to fullerene dominated at high concentrations in all the polyfluorene

derivatives. Furthermore, we found that exciton diffusion decreases when the side chain length changes from 8 to 12 carbon atoms. However, larger side groups can increase exciton diffusion.

The molecular structure of the polyfluorenes investigated in this study is shown in **Figure 1**. The top three molecules are named on the basis of alkyl side chain length. PFDP has the same backbone, but phenyl groups on the bridging carbon atoms, each with *t*-butyl groups attached. Boc-PF12 is a random copolymer fluorene units with either dodecyl sidegroups or *t*-butyloxycarbonyl (BOC) protected aminohexyl side group. The absorption and photoluminescence (PL) spectra are given in Figure 2a. All materials show a strong π - π^* absorption peaking in the range 382-395 nm. The absorption spectrum of PF15 is redder than the other materials, whilst that of PFDP is bluer. The PL spectra of all polyfluorene derivatives is dominated by a peak very close to 423 nm, with a further peak around 447 nm and a shoulder around 480 nm. This emission is characteristic of the glassy phase of polyfluorene.^[20-22] We measured the solid-state photoluminescence quantum yield (PLQY) using an excitation wavelength of 375 nm and the results are given in **Table 1**. All the samples are fluorescent with PLQYs ranging from 36% to 52%. We measured time-resolved fluorescence of neat films of material, and the time for the emission to fall to 1/e of its initial value was in the range 290-364 ps (Table 1). These values are similar to previously reported values of 250-360 ps for the lifetime in a film of polyfluorene with glassy phase^[22, 23].

In order to investigate the effect of side chain length on exciton diffusion, we measured time-resolved fluorescence decays of the blends of polyfluorene with small, known quantities of fullerene (PC₆₁BM). The resulting fluorescence decays are plotted in **Figure 2b and S1** as a function of the concentration of fullerene quencher. We observe that fluorescence decays get faster with increasing concentration of quencher. Furthermore, we observe (Figure S1) that for a given concentration of quencher (e.g. 0.5 wt%), fluorescence decays are slower in PF12 compared to the other polyfluorene derivatives, thus suggesting lower exciton diffusion in PF12. In contrast, PF15 has the fastest fluorescence decay among all of them, and hence highest

exciton diffusion. The PF8 and boc-PF12 show similar PL quenching for a given concentration of fullerene and so will have similar exciton diffusion constants.

To get quantitative information about exciton diffusion, we analysed the time-resolved data. Due to significant overlap between the absorption of quencher (PC₆₁BM) and PL of the donor (polyfluorene), there is a chance of direct quenching due to FRET. Therefore in order to get information about the rate of FRET and exciton diffusion coefficient, we split our analysis into regimes of lower and higher concentration of quencher^[2, 24-26] depending whether the rate of quenching is limited by Förster process or by diffusion. First, we consider the regime of higher concentration of the quencher, known as static quenching regime where the rate of quenching is limited by direct FRET to the acceptor. In this regime, photogenerated excitons are very close to acceptor molecules i.e. within a quenching radius. Therefore, the rate of quenching in this regime can be described by the following equation^[27]

$$\ln(PL\ ratio) = -\frac{4}{3}\pi N \left[\frac{\pi R_0^6 t}{\tau} \right]^{1/2} \quad (1)$$

where

$$PL\ ratio = \frac{PL_{quenched}}{PL_{unquenched}} \quad (2)$$

$PL_{quenched}$ is the PL intensity of the blend of polyfluorene with PC₆₁BM and $PL_{unquenched}$ is the PL intensity of neat polyfluorene. R_0 is the Förster radius, τ is the fluorescence lifetime of the material and N is the concentration of the quencher. We used equation 1 to fit the time-resolved fluorescence decays of blends with a quencher concentration of 5 wt% (Figure 3a). For convenience, we plotted the natural logarithms of the ratio of PL decays with respect to the square root of the time. From the fit, we obtained the value of Förster radii of $R_0 = 3.4$ nm, $R_0 = 3.0$ nm, $R_0 = 3.4$ nm, $R_0 = 3.6$ nm and $R_0 = 3.7$ nm for PF8, PF10, PF12, boc-PF12 and PF15 respectively.

For determination of the exciton diffusion coefficient, we used data at low concentrations of quencher (1 wt% and lower), so that quenching is controlled by exciton diffusion to the acceptor. In this regime, the quenching occurs when an exciton is within a certain radius r_F of the quencher which depends on exciton diffusivity and Förster radius^[27]. This rate of quenching can be extracted by taking the derivative of the natural logarithm of the ratio of quenched to unquenched films i.e.^[28, 29]

$$\frac{dPL_{quenched}}{dt} = -k(t)PL_{quenched} - k_q(t)PL_{quenched} \quad (3)$$

$$\frac{dPL_{unquenched}}{dt} = -k(t)PL_{unquenched} \quad (4)$$

By combining equation 2, 3 and 4, we get

$$k_q(t) = -\frac{d\ln(PL \text{ ratio})}{dt} \quad (5)$$

where PL ratio is as defined in equation 2

The diffusion coefficient is then obtained from the interpolation formula described by Gösele et al^[30, 31],

$$\ln(PL \text{ ratio}) = -4\pi D r_F N t - \frac{4}{3} \pi N \left[\frac{\pi R_0^6 t}{\tau} \right]^{1/2} \quad (6)$$

where

$$r_F = 0.676 \left[\frac{R_0^6}{D\tau} \right]^{1/4}$$

therefore as $t \rightarrow \infty$, equation 6 becomes

$$\ln(PL \text{ ratio}) = -4\pi D r_F N t \quad (7)$$

From equation 5 and 7, the rate of quenching $k_q(t)$ is given by

$$k_q(t) = -2.70\pi D \left[\frac{R_0^6}{D\tau} \right]^{1/4} N \quad (8)$$

The above equation (8) shows that at lower concentrations of the quencher and at long times, the rate of quenching is time independent. We determine this rate of quenching experimentally by taking the gradient of the natural logarithm of the ratio of quenched to unquenched films after 150 ps when the $\log(\text{ratio})$ s become linear (Figure 3b). The obtained values of the rate of quenching are plotted in Figure 4 against the concentration of quencher. The linearity here between the rate of quenching and the concentration of quencher indicates there is no aggregation of the fullerene and is consistent with our past work which only saw a deviation from linearity above a concentration of 0.03 nm^{-3} .^[24]

The value of the diffusion coefficient in each polymer was then extracted by linearly fitting the data and using equation 8 along with the calculated values of R_0 . The extracted values of diffusion coefficient are given in Table 1. The diffusion coefficient decreases when the side chain length increases from 8 to 12 carbon atoms (i.e. PF8 and PF12). This can be explained by larger spacing of conjugated backbones in PF12 by longer side groups because the spectral overlap of fluorescence and absorption is very similar in both polymers. In contrast, we observe a substantial red-shift of the absorption peak in PF15 compared to the other polymers which indicates an increase in effective conjugation length and also increases spectral overlap of fluorescence and absorption. Both these changes favour higher exciton diffusivity which is observed experimentally. Similar behaviour has been reported in other conjugated molecules.^[10,11,16,19] The increase in effective conjugation length implies lower conformational disorder in PF15 which could be explained by the very high molecular weight of PF15. PFDP has a diffusion coefficient of $0.7 \times 10^{-3} \text{ cm}^2/\text{s}$ which is lower than PF8. This reduction could arise from the very bulky *t*-butylphenyl groups leading to a more disordered film. This in turn would be consistent with the blue-shifted absorption spectrum. *boc*-PF12 has higher diffusion coefficient than PF12. This must arise from it being an alternating copolymer with an additional functional group and so a possible explanation for the higher value of exciton diffusion is due to different molecular packing and film morphology.^[18, 19]

In conclusion, we measured exciton diffusion in several polyfluorene derivatives with different side groups. We showed that exciton diffusion decreases by a factor of 6 on going from PF8 to PF12, and explored the effect of other side groups. We also found that the reduction or enhancement of exciton diffusion had little effect on the PLQY of the materials. Hence, we show that diffusivity of excitons can be controlled by side groups without significantly affecting the PLQY of materials. These results are significant for LEDs and laser where lower exciton diffusion and high PLQY are needed.

Experimental Section

Materials Synthesis and Film formation: The materials were synthesized following previously reported procedures.^[32-35] Thin films were made by spin-coating the solution from chlorobenzene (15 mg/mL) at 1200 rpm for 60s inside a nitrogen glove box.

Absorption PL and PLQY measurements: Absorption spectra were measured using a Cary 300 UV-Vis spectrometer. PL spectra were measured using an Edinburgh Instruments FLS980 fluorimeter. The excitation wavelength of 375 nm was used for all spectra reported here. PLQY was measured using an integrating sphere^[36] in a Hamamatsu Photonics C9920-02 system, also exciting at 375 nm.

Exciton diffusion measurements: The time-resolved fluorescence was measured by exciting the sample with 100 fs light pulses at 400 nm and PL was detected at 470 nm using a Hamamatsu C6860 synchroscan streak camera which has a time resolution of ~2 ps.

Supporting Information

Supporting Information is available from the Wiley Online Library.

Research data supporting this work is available at <https://doi.org/10.17630/c6fa8480-c005-4d5a-bcd0-ae0d0b88b80c>

Acknowledgements

We acknowledge financial support from FP7 project “Laser Induced Synthesis of Polymeric Nanocomposite Materials and Development of Micro-patterned Hybrid Light Emitting Diodes (LED) and Transistors (LET)” – LAMP project (G.A. 247928). M.T.S, A.R and I.D.W.S

acknowledge support from the European Research Council (EXCITON grant 321305). I.D.W.S acknowledges a Royal Society Wolfson Research Merit Award. We are grateful to EPSRC for an equipment grant (EP/L017008/1).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figures

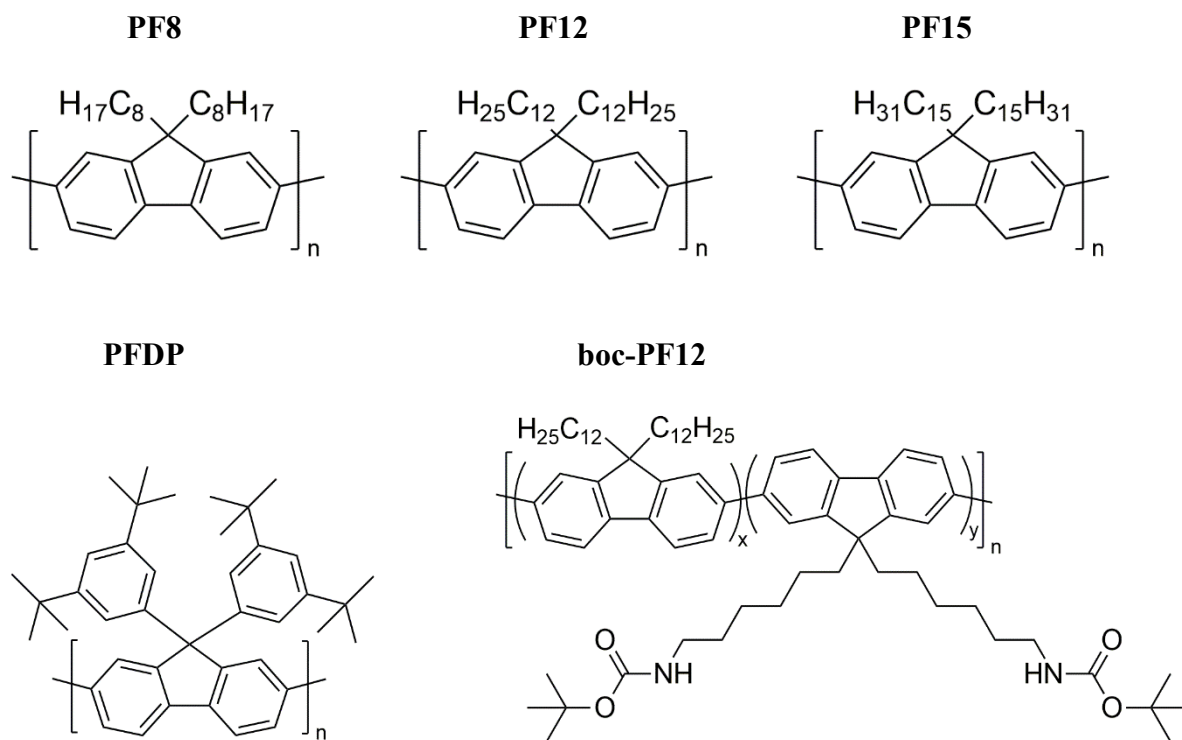


Figure 1: Molecular structures of polyfluorenes studied.

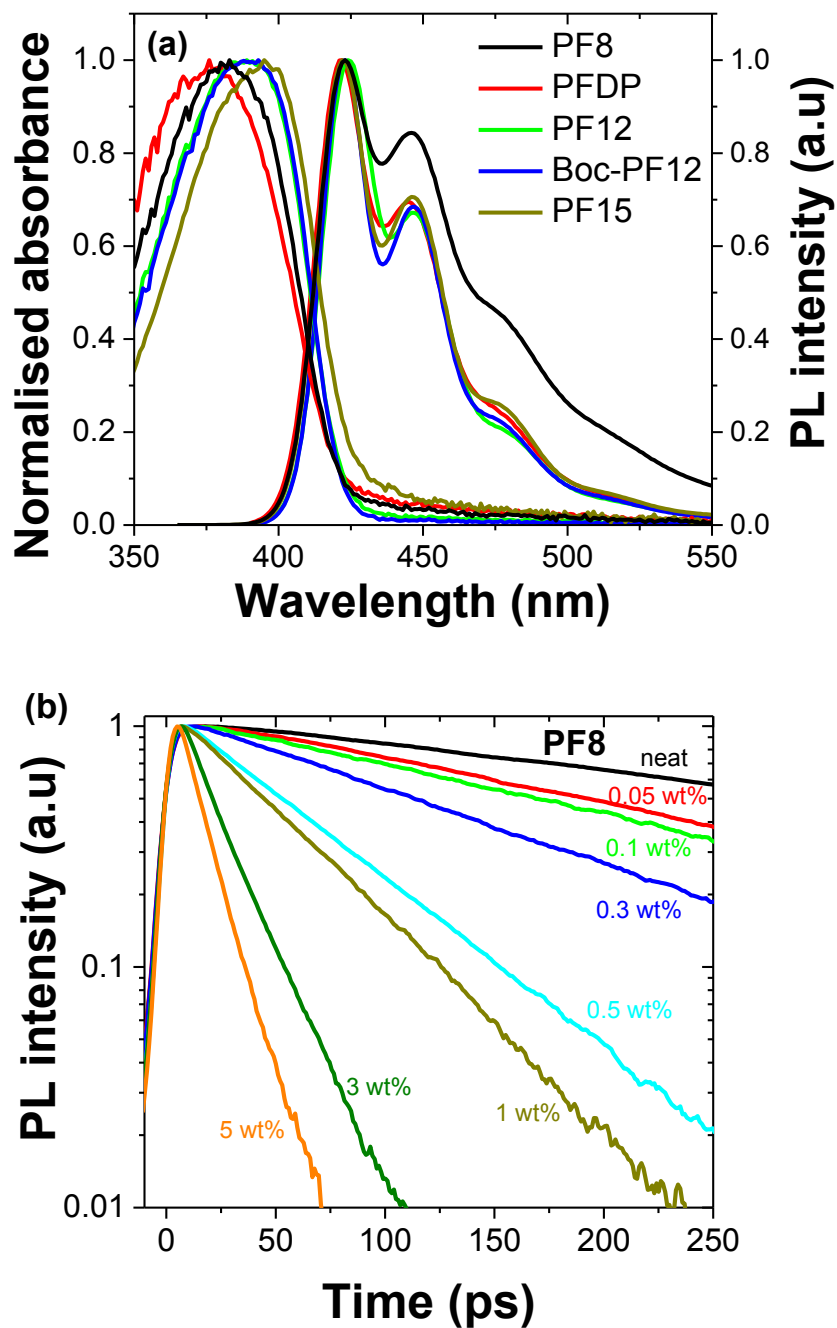


Figure 2: (a) Absorption and PL spectra. The PL was measured by exciting the thin films at 375 nm. (b) Time-resolved fluorescence measurements (excited at 400 nm) of neat PF8 and blends of PF8 with small known concentrations of PC₆₁BM.

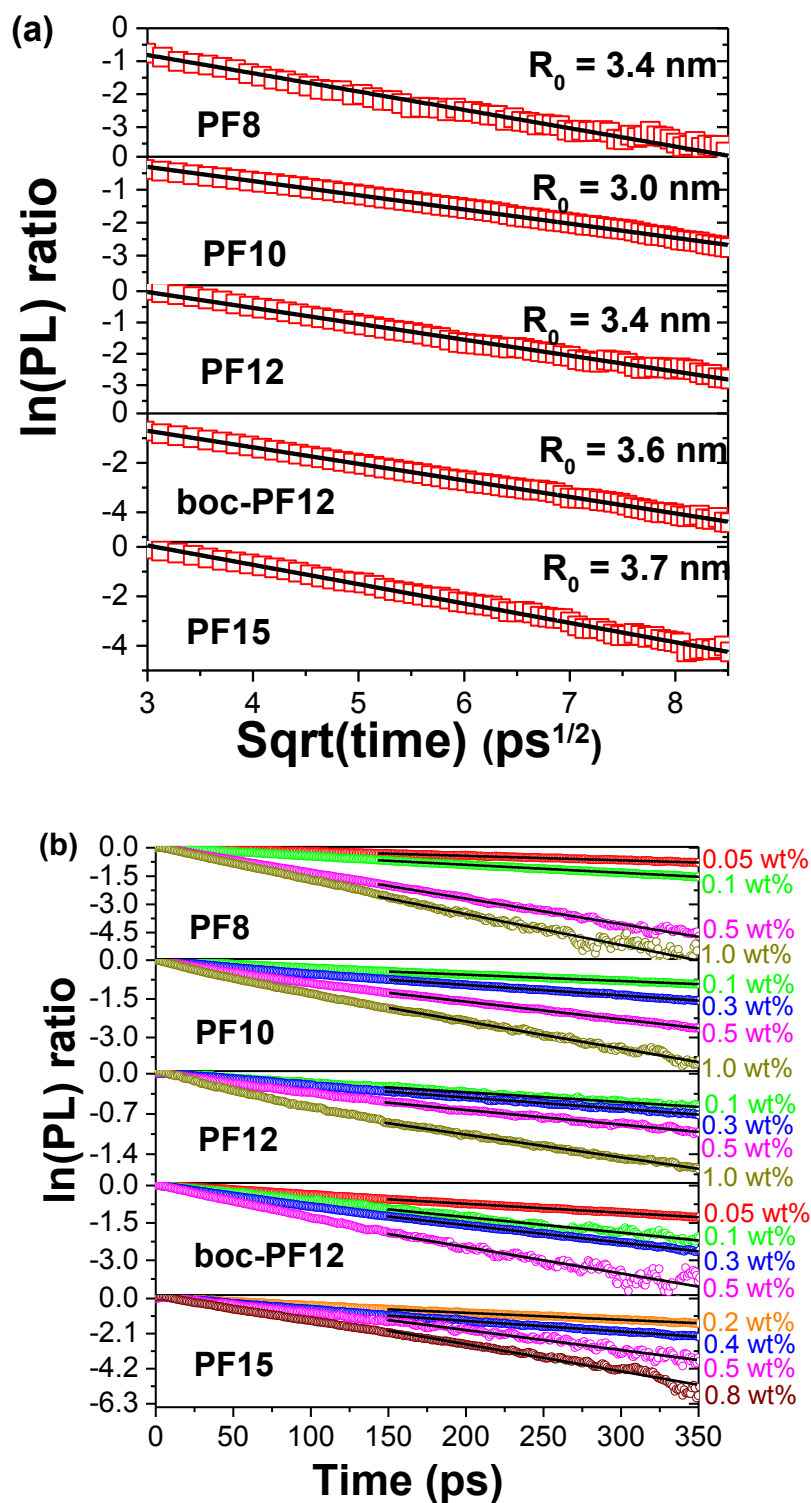


Figure 3: (a) The natural logarithm of the ratio of the PL with higher concentration of quencher (5 wt%) to the PL without quencher. The red lines are fits to the experimental data using equation (1), with the Förster radius, R_0 , as the fitting parameter. (b) The natural logarithms of the ratio of the PL with lower concentration of quencher (≤ 1 wt%) to the PL without quencher. Linear fits are also shown and their slope gives the rate of quenching (see text and equation 5).

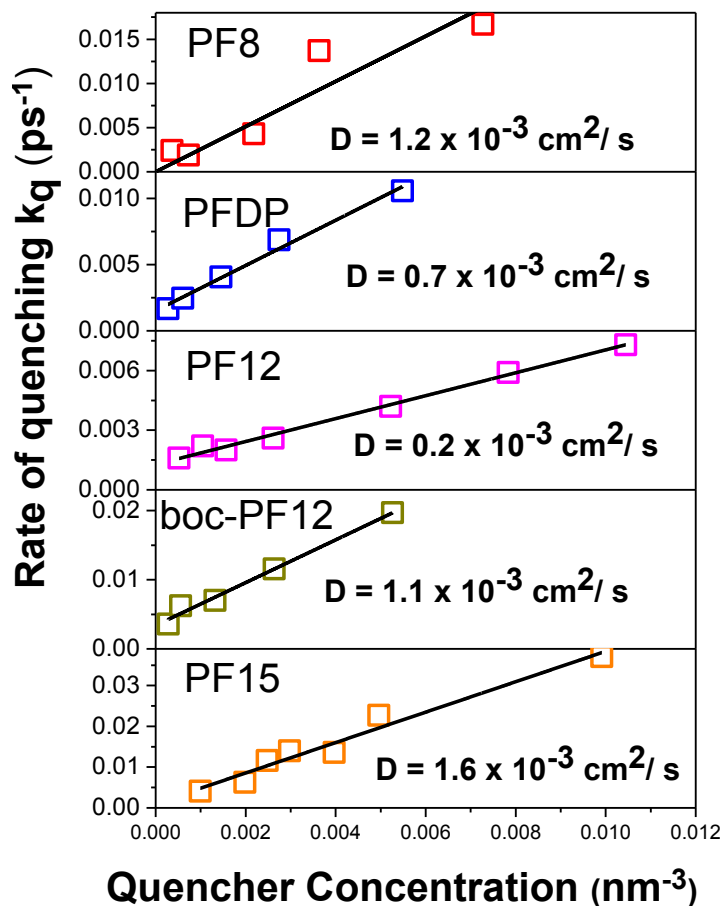


Figure 4: The rate of quenching $k_q(t)$, obtained from by taking the gradient of figure 2 after 150 ps, plotted as a function of concentration of the quencher. The red lines are linear fits, used along with previously determine value of forster radii (R_0) to determine diffusion coefficient in all polymers.

Table 1: Photoluminescence quantum yield (PLQY), PL lifetime measured when fluorescence falls to 1/e of initial value, exciton diffusion coefficient (D), number average molecular weight (M_n) and polydispersity (PD) of the polyfluorene derivatives studied.

Materials	PLQY (%)	1/e lifetime (ps)	D ($\times 10^{-4} \text{ cm}^2/\text{s}$)	M_n (g/mole)	PD
PF8	36 ± 1	364 ± 10	12.5 ± 1.2	135000	2,21
PFDP	38 ± 1	290 ± 10	7.0 ± 0.7	135000	2,86
PF12	49 ± 3	280 ± 10	2.0 ± 0.5	34200	1,97
boc-PF12	52 ± 1	340 ± 10	11.0 ± 1.1	45600	1,97
PF15	40 ± 1	325 ± 10	16.0 ± 1.6	351000	3,08