

Energy transfer in poly(3-hexylthiophene)-*g*-polyfluorene graft copolymers

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ABSTRACT

Conjugated graft copolymers consisting of a poly(3-hexylthiophene) (P3HT) backbone and poly(9,9'-dioctylfluorene) side-chains (PF) with different grafting degrees were synthesized by the CuAAC reaction. The properties of these materials were studied by UV-vis and fluorescence spectroscopy. The former technique provides insight in their self-assembly, while the latter is used to study the energy funneling from the PF side-chains to the P3HT backbone.

KEYWORDS: conjugated polymers; supramolecular structures; self-assembly; fluorescence; graft copolymers

INTRODUCTION

During last decade many materials involved in harvesting and transferring energy have been prepared. These systems consist of at least 2 conjugated systems and can adopt different topologies. By mimicking nature, dendrimers are the synthetic systems mainly used for energy harvesting.¹⁻³ These consist of a periphery of donor chromophores that funnel the energy to the central acceptor. Synthetically less challenging, consequently commercially more interesting, are conjugated polymers. Blends of conjugated polymers with certain dyes are especially exploited for biosensing.⁴⁻⁹ By using near infrared emission, *in vivo* imaging is even possible.¹⁰ Not only an energy transfer between a conjugated polymer and chromophore, but also intrachain energy transfer in conjugated polymers can occur.¹¹ For

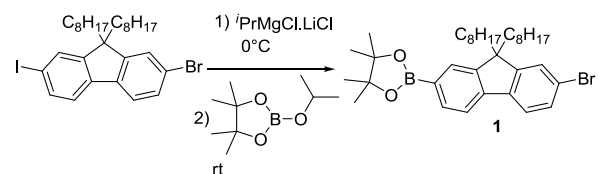
example, high efficiency white light luminescence can be obtained when fluorene is copolymerized with a small amount of a benzothiadiazole derivative.^{12,13} This energy transfer causes a redshift and a manifold increase of the polyfluorene (PF) luminescence. In triblock copolymers intrachain transfer can be exploited to investigate the order of the blocks.¹⁴ By even further modifying the conjugated polymers, structural analogs of dendrimers can be prepared. One possibility is transforming the end groups of hyperbranched conjugated polymers to a certain chromophore.¹⁵ Star-shaped conjugated copolymers contain an interesting topology as well in this context.¹⁰ In these materials, energy transfer takes place from the star arms to the core. Another category of very promising materials for light harvesting are conjugated

graft copolymers. The presence of the polymer side-chains will suppress aggregation of the luminescent polymer backbone and thereby improve the quantum efficiency, making them especially interesting for implementation in OLEDs.^{16,17} In contrast to dendrimers and hyperbranched polymers, by variation of the grafting density, the energy transfer from the “periphery” of side-chains to the backbone “core” can be controlled in order to obtain the desired material. Energy transfer has already been reported for graft copolymers consisting of a luminescent conjugated backbone polymer and non-conjugated side-chain polymers with pendant chromophores.^{16,17} However, energy transfer in all-conjugated graft copolymers has never been studied due to their challenging synthesis, although they are particularly interesting because in this case a polymer side-chain acts as a large antenna. Only two papers have been published reporting the synthesis of grafted all-conjugated polymers and this by the “grafting from” and “graft through” method.^{18,19} In this report, we describe the synthesis, self-assembly and emission characteristics of a series of all-conjugated graft polymers consisting of a poly(3-alkylthiophene) (P3AT) backbone and poly(dialkylfluorene) (PF) side-chains with different grafting degrees, synthesized by the “grafting-onto” method. Polythiophenes are interesting because of their high stability and processability. However, the most important drawback for implementation in PLEDs is their poor quantum efficiency. A polyfluorene was chosen as side-chain because of its high quantum efficiency and the fact that the emission spectrum overlaps with the absorption spectrum of polythiophene.

RESULTS AND DISCUSSION

Monomer synthesis

Monomer **1** for the synthesis of PF was obtained by adding 1 eq. of *i*PrMgCl.LiCl to 2-bromo-7-iodo-9,9-dioctyl-fluorene at 0°C.^{20,21,22} After 1 hour an excess of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and the mixture stirred for another 2 hours (Scheme 1).

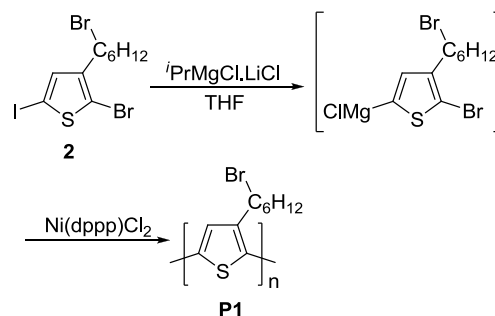


SCHEME 1 Synthesis of monomer **1**.

Precursor monomer **2** for the synthesis of P3AT was synthesized according to literature procedures.²³

Polymer synthesis

P3AT (**P1**) was obtained by polymerization of 2-chloromagnesio-5-bromo-(6-bromohexyl)-thiophene, in-situ prepared by a modified GRIM reaction on precursor monomer **2**, via Kumada couplings in the presence of Ni(dppp)Cl₂ (Scheme 2). After 1 hour the polymerization was quenched with acidified THF.



SCHEME 2 Synthesis of P3AT with 6-bromohexyl side-chains (**P1**).

The degree of polymerization (DP) is determined by the ratio of the ¹H-NMR signal

for the internal α -CH₂ (2.88-2.71 ppm) and the α -CH₂ (2.66-2.52 ppm) of the terminal units (FIGURE 1).²⁴ This results in DP=18, close to the DP aimed for (DP=20). GPC calibrated against polystyrene standards gave an \bar{M}_n -value of 5.9 kg/mol which corresponds to 24 monomer units. This is in line with the overestimation of the molar mass of conjugated polymers by this technique. Indeed using 1.3 as correction factor, DP=18 is obtained.²⁵

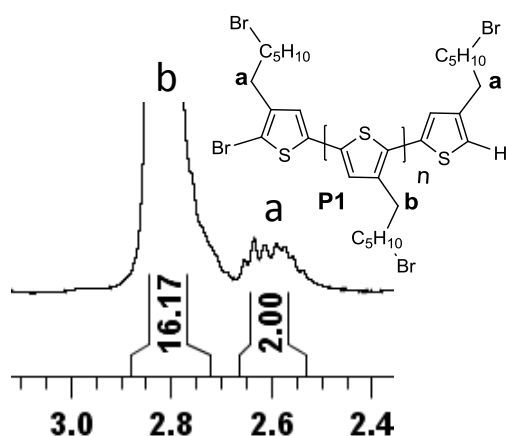
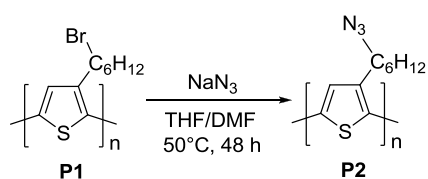


FIGURE 1 Integration of the signals of α -CH₂ of internal and external units in the ¹H-NMR spectra of **P1**.

In the final step, via a postpolymerization reaction, the bromine atoms are transformed into azide groups using sodium azide (Scheme 3).²⁶⁻²⁸



SCHEME 3: Postpolymerization reaction on **P1** substituting bromine groups for azide groups.

As expected the GPC analysis of **P2** delivers the same dispersity as **P1** (Table 2). FT-IR spectroscopy confirms the formation of the

alkylazide by appearance of a new peak at 2087 cm⁻¹. Also ¹H-NMR (FIGURE 2) and MALDI-ToF (Fig. 3) demonstrate a quantitative conversion.

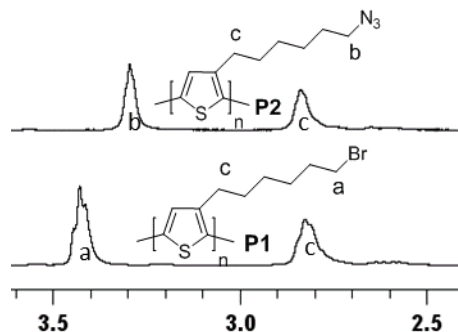


FIGURE 2 ¹H-NMR spectra of **P1** and **P2** in region 2.5-3.5 ppm, demonstrating quantitative conversion.

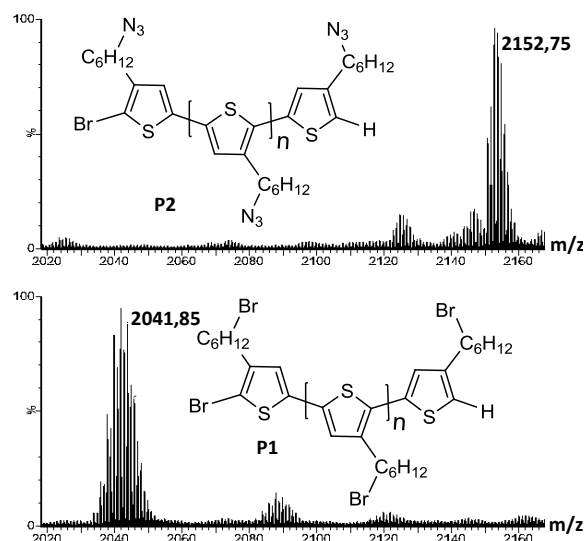
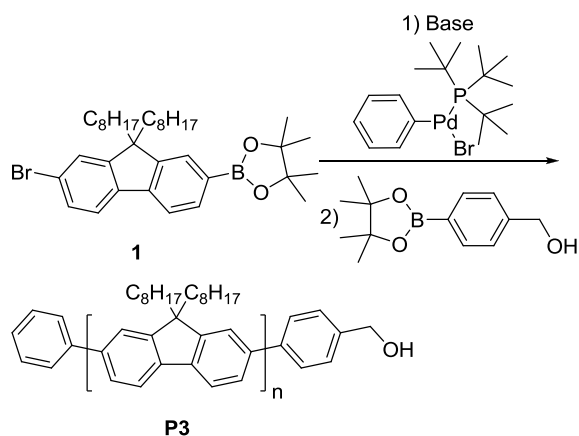


FIGURE 3 MALDI-ToF spectra of **P1** and **P2** demonstrating quantitative conversion.

The fluorene monomer **1** was polymerized via Suzuki couplings using the protocol developed by Yokozawa *et al.*^{22,29-31} The PhPd(PtBu₃)Br initiator was prepared *in situ*.^{10,31,32} To this initiator solution, a THF/H₂O solution of the monomer with 18-crown-6 and CsF was added at 0 °C. The polymerization of **P3** proceeded for 10 minutes after which the endcapper [4-

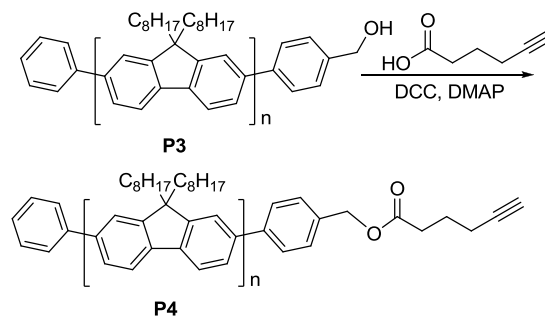
(4,4,5,5-tetramethyl-1,3,2-dioxaboron-2-yl)phenyl]methanol was added and the reaction was continued for 15 more minutes at 0°C (Scheme 4).^{33,34}



SCHEME 4 Polymerization of PF (**P3**) with phenyl initiator and termination with -OH functionalized endcapper.

GPC-analysis exhibits an \bar{M}_n -value of 11.8 kg/mol and a dispersity of 1.8. Wang *et al.* determined the correction factor for the real \bar{M}_n -values of PF.³⁵ By applying this correction factor an \bar{M}_n -value of 6.9 kg/mol is obtained. This \bar{M}_n -value corresponds with a chain length of 18 units. In order to identify the nature of the end-groups, MALDI-ToF spectra were recorded (SI, S13).³⁶ Although the protocol developed by Yokozawa *et al.* is expected to lead to a controlled polymerization with defined end-groups, this was not observed. Not only polymers with the phenyl initiator and endcapper built in are present, also polymers lacking one of the endgroups are present and a fraction of the polymers contains an endcapper at both sides. Although the presence of dicapped PF could in the following steps result in crosslinking (see further), no purification was performed as it is impossible to separate the polymers by endgroups.

In a further step a terminal acetylene function was introduced by performing a postpolymerization reaction, i.e. coupling hexynoic acid to the endcapper using the Steglich reaction (Scheme 5).^{37,32} The dispersity is 1.9 instead of 1.8. This can be understood because the polymers with 2 endcappers will react twice while a polymer that does not contain any endcapper will not elongate at all. MALDI-ToF shows that no hydroxyl terminated polymers are present in the sample (see SI, S14). Peaks could be assigned to polymers with one or two terminal acetylene functions.



SCHEME 5 Steglich postpolymerization reaction of **P3** with hexynoic acid.

This result is further supported by ¹H-NMR spectroscopy demonstrating a complete conversion of terminal hydroxyl functions into acetylene functions (Fig. 4).

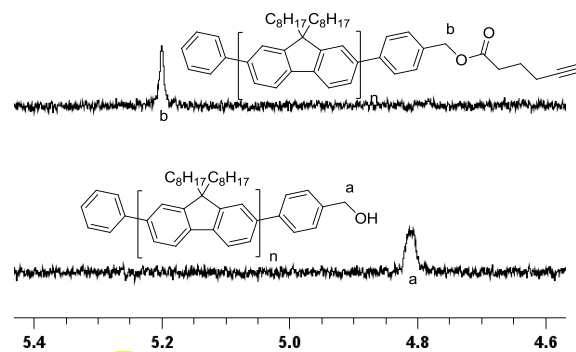
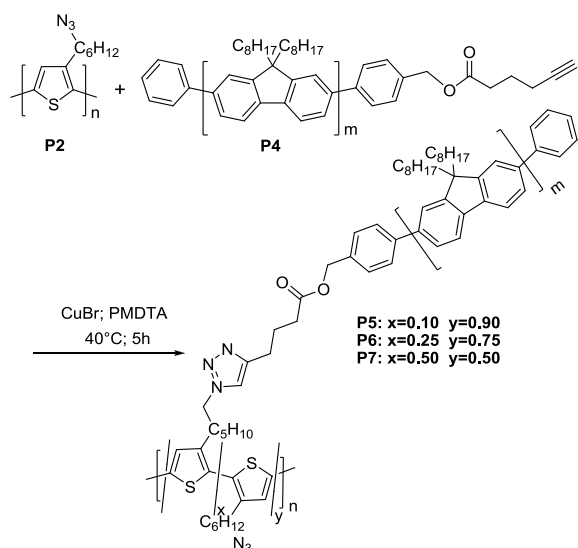


FIGURE 4 ¹H-NMR spectra of **P3** and **P4** in region 4.6–5.4 ppm, demonstrating quantitative conversion.

In the last step, after end-group modification with hexynoic acid, the PF side-chains were grafted to the P3AT backbone using the CuAAC click reaction with CuBr/PMDTA as catalyst system (Scheme 6). The high yields of this reaction should lead to a good control over the grafting density and enable us to reach high degrees of functionalization. This reaction is often reported for the preparation of graft copolymers by the “grafting to” method.^{38–42} By adjusting the ratio between P2 and P4, degrees of functionalization of 10, 25 and 50 were aimed for, resulting in P5, P6 and P7 respectively (Table 1). Although cross-linking could theoretically occur, no gel formation or precipitation of polymer was observed in the reaction mixture. To remove unreacted PF (P4), a Soxhlet extraction was performed with heptane. The small amount of P3AT (P2) still present in P5 was removed by preparative column.



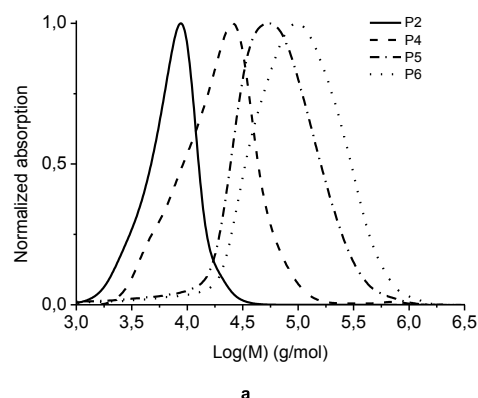
SCHEME 6 Grafting of PF side-chains to the P3AT backbone.

TABLE 1 Ratio polymers and catalysts used and yields for the “grafting to” reaction.

Polymer	#mg P2	#mg P4	mg CuBr	mg PMDTA	Yield (%)
P5	5	15.3	3.4	4.1	20
P6	3	23.0	2.1	2.5	18
P7	2	30.6	1.4	1.7	23

GPC, IR and NMR of the graft copolymers

After purification, gel permeation chromatography was performed. The chromatograms and corresponding molar masses and dispersities are displayed in Figure 5a and Table 2, respectively. There is a clear increase in molar mass upon increasing the ratio of PF (P4) to P3AT (P2). No measurements could be performed on polymer P7 as it becomes insoluble after precipitation. The dispersities of the graft copolymers are in the same range (Table 2). Consequently, a study of the influence of the grafting degrees on the properties can be performed.



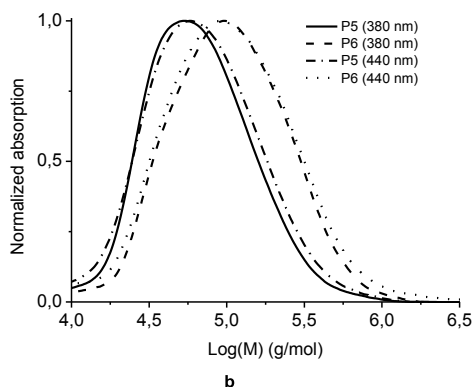


FIGURE 5 a) GPC spectra of homopolymers **P2** and **P4** and graft-copolymers **P5** and **P6**. b) GPC spectra of graft copolymers at 380 and 440 nm.

To prove the absence of homopolymer, the GPC measurement was performed with detection at two different wavelengths: 380 nm (λ_{\max} PF) and 440 nm (λ_{\max} P3AT) (Fig. 5b). The \bar{M}_n values and the dispersities are nearly identical and no homopolymers could hence be detected (Table 2).

TABLE 2: \bar{M}_n and PDI values of the homopolymers and graft-copolymers **P5** and **P6**.

Polymer	λ	\bar{M}_n (kg/mol)	\bar{D}
P1	440	5.9	1.3
P2	440	6.0	1.3
P3	380	11.8	1.8
P4	380	12.0	1.9
P5	380	43.5	1.8
P5	440	44.7	1.8
P6	380	63.9	1.9
P6	440	64.7	1.9

IR-spectra were recorded of the graft-copolymers. The signal corresponding with residual nonreacted azide groups is still visible,

in accordance with the $^1\text{H-NMR}$ spectra (SI S9-S10).

In order to check if the aimed degrees of functionalization correspond to the expected grafting degrees, a $^1\text{H-NMR}$ analysis was performed. To have a precise determination of the grafting percentages the integration values of the $-\text{CH}_2$ peaks of P3AT next to the thiophene unit (c) and the azide group (e) should be determined (Fig. 6). The grafting percentage is calculated as:

$$= \frac{\# \text{ azide functions (initial)} - \# \text{ azide functions (nonreacted)}}{\# \text{ azide functions (initial)}}$$

$$= \frac{c - e}{c}$$

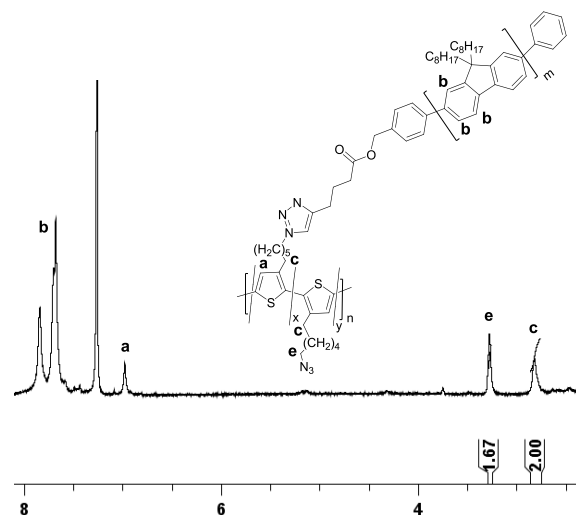


FIGURE 6 Analysis of the $^1\text{H-NMR}$ spectrum of **P6** in region of 2.5-8 ppm.

While targeting 10 and 25%, values of 10 and 17% were achieved. A lower percentage was nevertheless expected due to the fact that not all polyfluorene polymers are endcapped with an acetylene function and thus not undergoing the click reaction.

UV-Vis spectroscopy

UV-vis experiments were performed on both homopolymers (**P2** and **P4**) and the two graft-copolymers (**P5** and **P6**). In a first step the spectra in pure chloroform were studied (Fig. 7). We can clearly see the difference in λ_{\max} for both homopolymers **P2** (440 nm) and **P4** (380 nm). Also the higher P3AT content in the graft copolymer **P5** compared to **P6** is clearly visible. In this solvent the polymers are completely dissolved and behave independently of each other. Consequently these spectra allow to calculate the mass fractions of P3AT and PF in the graft copolymer using the spectra of **P2** and **P4** in 100% CHCl_3 . These mass fractions obtained via UV-vis nicely correlate with those derived from $^1\text{H-NMR}$ spectroscopy (Table 3).

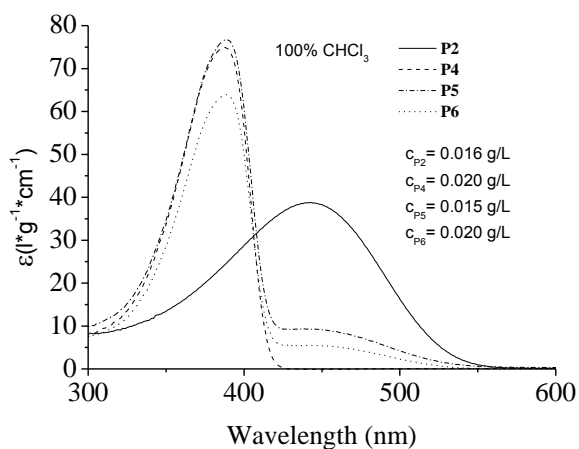


FIGURE 7 UV-vis spectra of homopolymers **P2** and **P4** and graft copolymers **P5-P6** in 100% CHCl_3 .

To study the aggregation behavior of these polymers, ten solutions were made with an increasing ratio of the nonsolvent methanol to chloroform (SI, S15-18). From this experiment we can conclude that P3HT aggregates from 50% MeOH (see SI, S15), indicated by the occurrence of a clear redshift. PF aggregates

already from 40% MeOH (see SI, S16). This is only visible by the appearance of an extra peak around 440nm.⁴³

It is known for block copolymers that the block stacking first when adding nonsolvent can influence the stacking of the second block, causing it to stack differently as when it is a homopolymer.⁴⁴ This phenomenon will be investigated for our case in which we have the conjugated backbone as “one block” and the PF sidechains as the first aggregating “other block”. For this we did a simulation of the spectra in MeOH/ CHCl_3 (90/10) mixture. In this mixture the polymers are in the aggregated state, but do not yet flocculate. It is therefore the most suited mixture to study the aggregation behavior. For this simulation, the spectra of the graft copolymers were modeled as a linear combination of the spectra of the 2 homopolymers **P2** and **P4** in 90% MeOH. The contribution factor of each block corresponds with the mass fraction determined via the spectra in pure chloroform (Table 3).

TABLE 3 Mass percentages of P3AT and PF in the graft copolymer **P5** and **P6** determined via $^1\text{H-NMR}$ and UV-vis spectroscopy.

Polymer	NMR PFm%	NMR P3ATm%	UV-vis PFm%	UV-vis P3ATm%
P5	73	27	74	26
P6	83	17	86	14

For all graft copolymers the peak around 600 nm, originating from the stacking of the P3AT, is less pronounced in the experimental spectra compared to the simulated spectra (Fig. 8). This less pronounced fine structure can be explained due to the fact that PF chains self-assemble first and thus impart the stacking of P3AT, covalently bonded to PF.

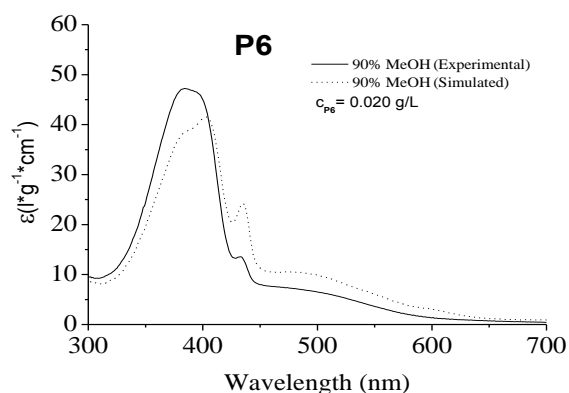
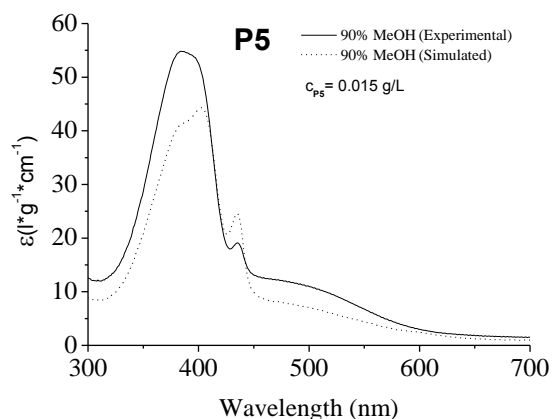


FIGURE 8 Experimental vs simulated UV-vis spectra of graft copolymers **P5-P6** in 90% MeOH.

Fluorescence spectroscopy

Fluorescence was measured for solutions of the polymers in pure chloroform. The excitation wavelength was 380 nm. Note that the $\lambda_{\max,em}$ for the PF side-chains is around 420 nm, while the $\lambda_{\max,abs}$ of the P3AT side-chains is around 440 nm (Fig. 9). This close overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor should allow an efficient energy transfer.

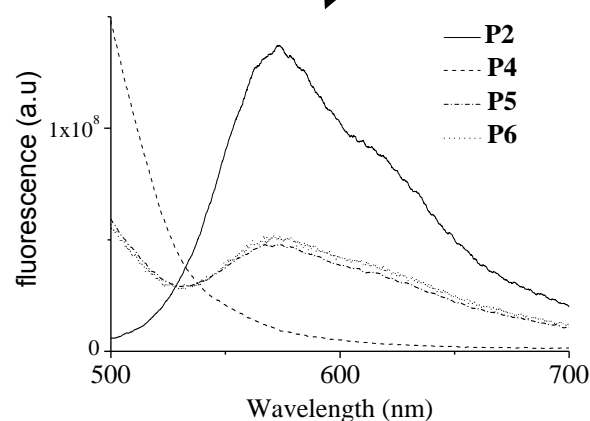
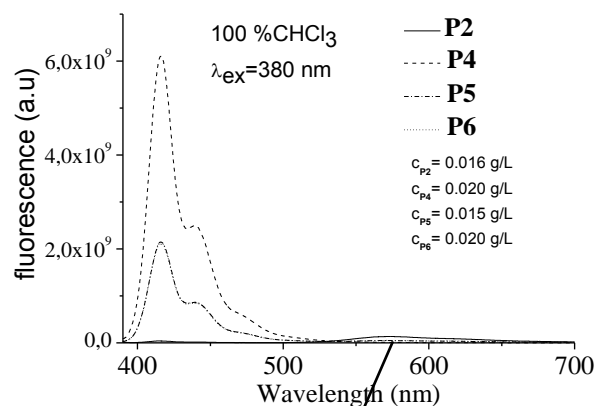


FIGURE 9 Fluorescence spectra, corrected for absorption at excitation wavelength, of homopolymers **P2** and **P4** and graft copolymers **P5-P6** in 100% CHCl₃.

A first look at the fluorescence spectra, corrected for absorption at excitation wavelength, shows a dramatic decrease of the fluorescence of the PF side-chains for both graft copolymers. The amount of quenching and transfer to P3AT backbone was calculated (Table 4). The mass fractions of P3AT and PF, calculated from the mole fractions by NMR, together with the spectra of the homopolymers, allows to calculate the fluorescence in absence of energy transfer.

TABLE 4 Difference in fluorescence (corrected for absorption at excitation wavelength) of the PF side-chains and P3AT backbone in graft copolymers **P5** and **P6**.

	Difference in Fluorescence (%)	
	P5	P6
PF side-chains	-52	-58
PT backbone	28	113

According to the calculations, the fluorescence of the PF is strongly decreased, while the fluorescence of the PT backbone is strongly increased. While the decrease of the PF fluorescence could also be attributed to concentrational or conformational quenching, this cannot explain the increase of the PT fluorescence. Combined, these results point at energy transfer from the PF side-chains to the PT backbone. The comparison between **P5** and **P6** reveals that the energy transfer is more severe in case the grafting density increases.

CONCLUSION

All-conjugated graft copolymers, composed of a P3AT backbone and PF sidechains, were synthesized by the “grafting to” method. This was achieved by the CuAAC click reaction of alkyne end-capped PF to azido-functionalized P3AT. GPC demonstrates the synthesis of graft copolymers with an increasing grafting density and absence of homopolymer. By ¹H-NMR analysis, grafting percentages of 10 and 17% were determined for **P5** and **P6**. When aimed for a grafting percentage of 50%, the graft copolymers were not soluble anymore. The aggregation behavior was studied by comparing the experimental and simulated UV-vis spectra. This indicated that the stacking of the P3AT backbone is compromised due to the stacking

of the PF side-chains that self-assemble first. To study energy transfer, fluorescence spectra were recorded for both homo- and graft copolymers. When the PF side-chains are excited, energy transfer to the P3AT backbone takes place. This transfer increases upon increasing the grafting degree.

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GRAPHICAL ABSTRACT

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Energy transfer in P3HT-*g*-PF graft copolymers

A series of all-conjugated graft copolymers with an increasing degree of grafting were prepared. By comparing the experimental UV-vis spectra with spectra simulated on basis of the homopolymers the influence on the self assembly of these materials was investigated. Using fluorescence spectra energy funneling from the PF side-chains to the P3AT “core” was demonstrated.

