



# The synthesis and spectroscopic characterization of poly(*p*-phenylene ethynylene) with 3-connected BODIPY end groups

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## ABSTRACT

A novel 3-connected BODIPY end-capped poly(*p*-phenylene ethynylene) and a matching model compound were synthesized by palladium-catalyzed cross-coupling reaction. The structures were confirmed using <sup>1</sup>H NMR, UV–vis spectrophotometry and fluorescence spectroscopy. Both the polymer and the model compound showed absorption and emission bands characteristic for the BODIPY chromophore and the *p*-phenylene ethynylene linker. However, while upon excitation of the *p*-phenylene ethynylene linker energy transfer occurs for nearly 100% in the model compound, it is only a minor decay channel of the singlet excited state of the *p*-phenylene ethynylene linker in the polymer.

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## 1. Introduction

In the past decades, there has been a vast increase in the research and application of conjugated polymers. Particularly, poly(phenylene ethynylene)s (PPEs) have attracted considerable interest due to their easy synthesis via the Sonogashira cross-coupling methodology, and interesting properties resulting from their linear structure and strong fluorescence [1–3]. As promising materials, PPEs have been applied widely in chemo- and biosensors [2,3] and electronic devices such as Organic Light Emitting Diodes (OLEDs) [4,5], Organic Field Effect Transistors (OFETs) [6] and solar cells [7,8].

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) derivatives are interesting dyes because of their advantageous characteristics, such as sharp absorption and fluorescence bands in the visible wavelength range, reasonably high fluorescence quantum yields, relatively large molar absorption coefficients, and robustness against light and chemicals [9,10]. All of these features stimulate their applications as fluorescent chemosensors [11–15], light-harvesting systems [16–18], fluorescent labels [19], and in some cases potential sensitizers in photodynamic therapy [20].

Covalent incorporation of BODIPY into PPE can efficiently tune the photophysical properties of conjugated polymer systems [21–25]. Chujo et al. have reported the preparation of highly fluorescent PPE polymers containing BODIPY, which can self-assemble into particles, fibers, and network structures by intermolecular  $\pi$ – $\pi$  stacking of BODIPY [21]. Also, a series of color-tunable PPE polymers with narrow emission band have been synthesized by attaching them directly to the BODIPY cores to extend the  $\pi$ -conjugation of the PPE polymers [23–25]. Furthermore, Li et al. have reported that the BODIPY component in polymers can enhance the nonlinear optical properties of the PPE polymer [22].

As an addition to these intriguing systems, here we report the design and synthesis of BODIPY end-capped PPE and its optical properties. Such a BODIPY end-capped PPE polymer can offer a model to study the energy transfer along the rigid chain and help one to design novel PPE polymers useful for optical and electronic applications.

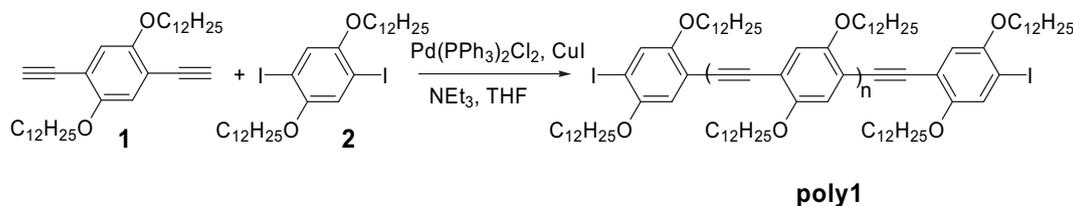
## 2. Experimental

### 2.1. Materials

1,4-Diethynyl-2,5-bis(dodecyloxy)benzene (**1**) and 1,4-diiodo-2,5-bis(dodecyloxy)benzene (**2**) were synthesized according to

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Scheme 1. Synthetic route to **poly1**.

literature procedures [26]. Bis(triphenylphosphine)palladium(II) chloride [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and CuI were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium prior to use.

## 2.2. Instrumentation

<sup>1</sup>H NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz. GPC measurements with linear PS standard calibration were performed on a Shimadzu apparatus using PLgel mixed-D columns (Polymer Laboratories) at 1 mL/min at 30 °C. All the polymer solutions were prepared in THF (ca. 2 mg/mL) and filtered through 0.45- $\mu$ m PTFE syringe-type filters before being injected into the GPC system.

UV–vis absorption spectra were recorded on a Perkin Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state excitation and emission spectra were obtained using an SPEX Fluorolog. For the determination of the relative fluorescence quantum yields ( $\Phi_f$ ) in solution (THF and toluene), only dilute solutions with an absorbance below 0.1 at the excitation wavelength  $\lambda_{ex}$  were used. Acridine yellow in methanol ( $\Phi_f = 0.57$ ,  $\lambda_{ex} = 420$  nm) and cresyl violet in methanol ( $\Phi_f = 0.55$ ,  $\lambda_{ex} = 550$  nm) were used as fluorescence standards. In all cases, correction for the solvent refractive index was applied. All spectra were recorded at 20 °C using undegassed samples.

## 2.3. Synthesis

### 2.3.1. Poly(*p*-phenylene ethynylene) with iodide terminal groups (**poly1**, Scheme 1)

490 mg (1 mmol) 1,4-diethynyl-2,5-bis(dodecyloxy)benzene (**1**) and 694 mg (1 mmol) 1,4-diiodo-2,5-bis(dodecyloxy)benzene (**2**) were dissolved in 15 mL of THF and 1 mL of Et<sub>3</sub>N under argon. To this solution 14 mg (0.02 mmol) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 4 mg (0.02 mmol) CuI were added. The reaction mixture was heated at 60 °C for 24 h. Then, 69 mg (0.1 mmol) of **2** was added and reacted for another 3 h to ensure that at the end of polymerization the polymer chain was terminated by iodine atoms. After the reaction mixture was cooled to room temperature, insoluble solids were

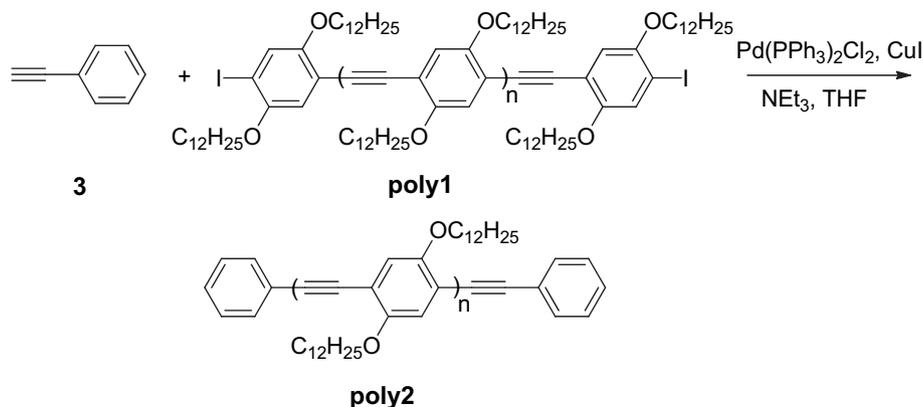
filtered off. The soluble filtrate was concentrated to 3 mL, and added dropwise into 60 mL of methanol and acetone (4:1, v/v) under stirring to precipitate the polymer. Then the product was redissolved in 3 mL of THF, and added dropwise through a cotton filter into 60 mL of methanol and acetone (4:1, v/v). The dissolution-precipitation process was repeated three times, and the final, isolated precipitate was dried under vacuum at 40 °C to a constant weight (575 mg, 62% yield).  $M_w$  16 100;  $M_w/M_n$  2.0 (GPC, polystyrene calibration). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.30, 7.02–6.89 (br, 2H, Ar–H), 4.01 [br, 4H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>], 1.83 [br, 4H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>], 1.51 [br, 4H, O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>], 1.26 [br, 32H, O(CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>], 0.87 [br, 6H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>].

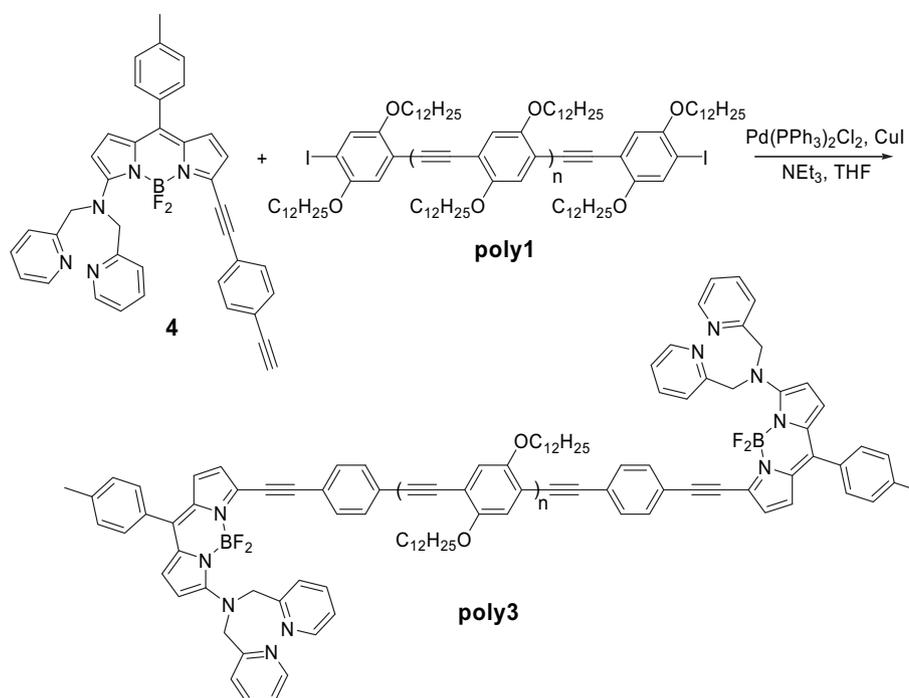
### 2.3.2. Poly(*p*-phenylene ethynylene) with phenyl terminal groups (**poly2**, Scheme 2)

50 mg **poly1** and 11  $\mu$ L (0.1 mmol) phenylacetylene (**3**) were dissolved in 10 mL of THF and 0.3 mL of Et<sub>3</sub>N under argon. To this solution 1 mg (1.4  $\mu$ mol) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 0.2 mg (1  $\mu$ mol) CuI were added. The reaction mixture was heated at 60 °C for 48 h. After the reaction mixture was cooled to room temperature, the solution was concentrated. The residue was washed three times with acetone, and dried under vacuum at 40 °C to a constant weight (44 mg, 88% yield).  $M_w$  15 700;  $M_w/M_n$  2.1 (GPC, polystyrene calibration). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.53, 7.33, 7.02–6.89 (br, 2.8H, Ar–H), 4.02 [br, 4H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>], 1.83 [br, 4H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>], 1.52 [br, 4H, O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>], 1.25 [br, 32H, O(CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>], 0.87 [br, 6H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>].

### 2.3.3. Poly(*p*-phenylene ethynylene) with BODIPY terminal groups (**poly3**, Scheme 3)

The synthesis and characterization of 5-*N*-(2-picolyl)amine-4,4-difluoro-3-(4-(ethynyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**4**), which is used in the synthesis of **poly3** (Scheme 3) and model compound **5** (Scheme 4) will be described elsewhere [27]. 50 mg **poly1** and 4 mg (6.6  $\mu$ mol) of **4** were dissolved in 10 mL of THF and 0.3 mL of Et<sub>3</sub>N under argon. To this solution 1 mg (1.4  $\mu$ mol) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 0.2 mg (1  $\mu$ mol) CuI were added. The reaction mixture was heated at 60 °C for 48 h. After

Scheme 2. Synthetic route to **poly2**.



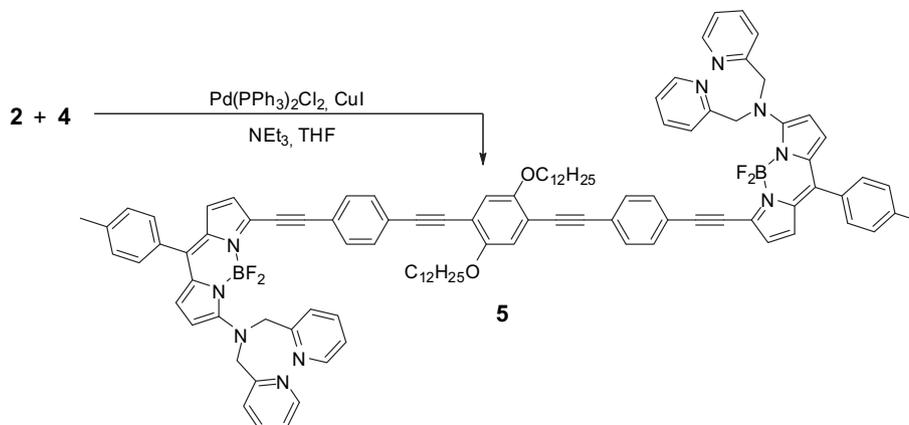
Scheme 3. Synthetic route to poly3.

evaporating the solvent, the crude product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 40$  mL), dried over  $\text{MgSO}_4$ , and  $\text{CH}_2\text{Cl}_2$  was evaporated under reduced pressure. The residue was washed three times with acetone until the solution was colorless. The obtained solid was further purified by column chromatography on silica gel, first eluting with a mixture of  $\text{CH}_2\text{Cl}_2$  and ethyl acetate (1:1, v/v) and followed by a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol (5:1, v/v) to give poly (*p*-phenylene ethynylene) capped with BODIPY end groups (17 mg, 35% yield).  $M_w$  13 300;  $M_w/M_n$  1.3 (GPC, polystyrene calibration).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.56, 7.79–7.28, 7.08–6.81 (br, 2.7H, Ar–H), 5.30 [br, 0.24H,  $\text{N}(\text{CH}_2)_2$ ], 4.01 [br, 4H,  $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$ ], 2.43 (br, 1.8H, Ar $\text{CH}_3$ ), 1.84 [br, 4H,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ], 1.51 [br, 4H,  $\text{O}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_8\text{CH}_3$ ], 1.25 [br, 32H,  $\text{O}(\text{CH}_2)_3(\text{CH}_2)_8\text{CH}_3$ ], 0.87 [br, 6H,  $\text{O}(\text{CH}_2)_{11}\text{CH}_3$ ].

#### 2.3.4. Model compound 1,4-bis((4-((5-*N*-(2-picolyl)amine-4,4-difluoro)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene-3-yl)ethynyl)phenylethynyl)-2,5-bis(dodecyloxy)benzene (5, Scheme 4)

60 mg (0.1 mmol) of **4** and 35 mg (0.05 mmol) of **2** were dissolved in 16 mL of THF and 0.3 mL of  $\text{Et}_3\text{N}$  under argon. To this

solution 3.5 mg (5  $\mu\text{mol}$ )  $\text{PdCl}_2(\text{PPh}_3)_2$  and 1 mg (5  $\mu\text{mol}$ )  $\text{CuI}$  were added. The reaction mixture was heated at 60  $^\circ\text{C}$  for 20 h. After evaporating the solvent, the crude product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 40$  mL), dried over  $\text{MgSO}_4$ , and  $\text{CH}_2\text{Cl}_2$  was evaporated under reduced pressure. Purification was preformed by chromatography on silica gel with a mixture of  $\text{CH}_2\text{Cl}_2$  and ethyl acetate (1:1, v/v), followed by a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol (1:10, v/v) to give **5** (40 mg, 48% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.56 (d, 4H,  $J = 4.6$  Hz, pyridine-6), 7.68 (t, 4H,  $J = 7.3$  Hz, pyridine-4), 7.45 (m, 12H), 7.34 (d, 4H,  $J = 7.3$  Hz), 7.21 (m, 8H), 7.01 (s, 2H), 6.84 (d, 2H,  $J = 4.9$  Hz), 6.60 (d, 2H,  $J = 3.7$  Hz), 6.36 (d, 2H,  $J = 4.9$  Hz), 6.29 (d, 2H,  $J = 3.7$  Hz), 5.30 (s, 8H), 4.04 [t, 4H,  $J = 6.4$  Hz,  $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$ ], 2.42 (s, 6H,  $\text{CH}_3$ ), 1.86 [m, 4H,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ], 1.54 [m, 4H,  $\text{O}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_8\text{CH}_3$ ], 1.25 [m, 32H,  $\text{O}(\text{CH}_2)_3(\text{CH}_2)_8\text{CH}_3$ ], 0.87 [m, 6H,  $\text{O}(\text{CH}_2)_{11}\text{CH}_3$ ].  $^{13}\text{C}$  NMR (75 Mz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 164.2, 156.4, 153.6, 149.5, 139.2, 137.0, 136.3, 135.4, 133.8, 131.9, 131.8, 131.3, 130.4, 128.9, 125.5, 123.6, 122.7, 121.9, 121.3, 120.5, 119.3, 116.9, 115.3, 114.0, 95.4, 95.1, 87.8, 86.0, 69.6, 58.1, 31.9, 29.7, 29.4, 26.0, 22.7, 21.4, 14.2. ESI-MS:  $m/z$  1672.7  $[\text{M} + \text{Na}]^+$ .



Scheme 4. Synthetic route to 5.

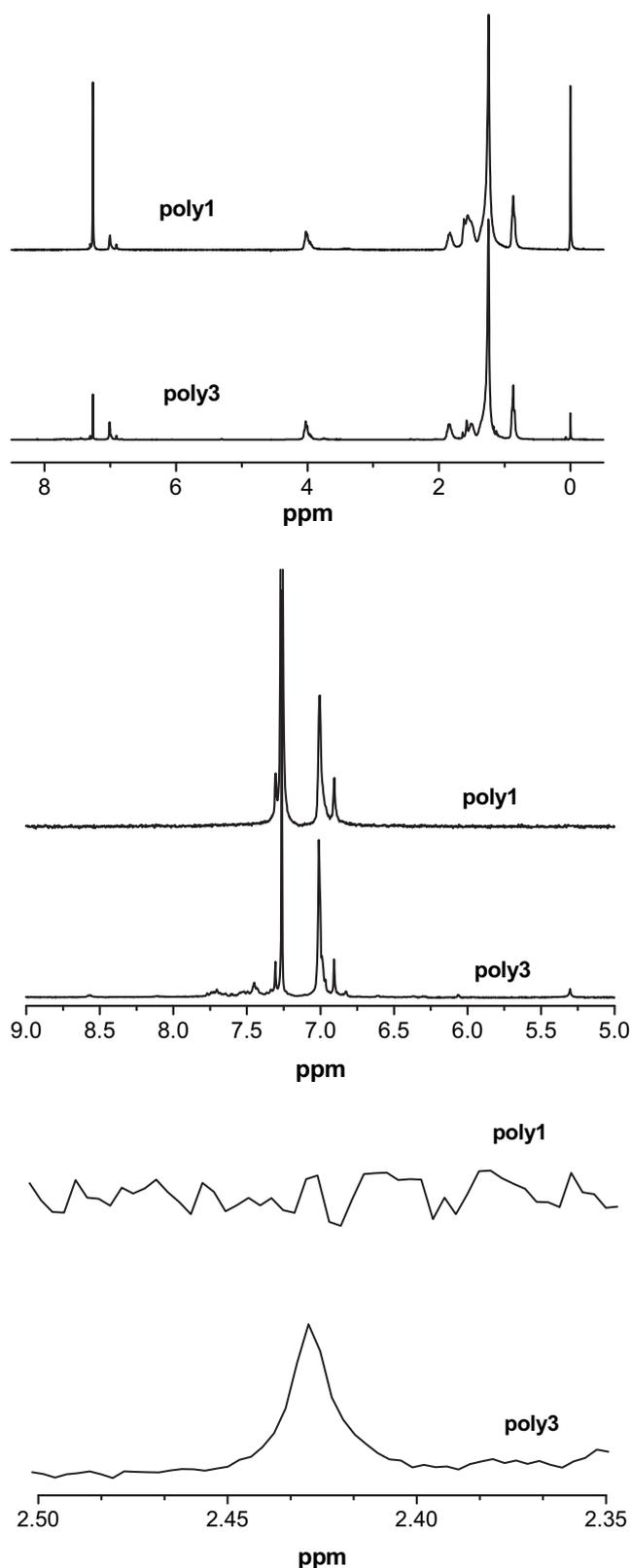


Fig. 1.  $^1\text{H}$  NMR spectra of **poly1** and **poly3** in  $\text{CDCl}_3$ .

### 3. Results and discussion

#### 3.1. Synthesis

The synthesis of **poly3** is highlighted in Scheme 3. The initially formed **poly1** ( $M_w$  of 16 100 and polydispersity index (PDI) of 2.0) was end-capped by reacting it with an excess of the ethynyl substituted BODIPY **4**. After washing several times with acetone, **poly3** was further purified by column chromatography to ensure that **poly3** was terminated by fluorophore **4**. The  $M_w$  of **poly3** is 13 300 and PDI is 1.3. As a result of the chromatography higher molecular weight fractions were removed, yielding a narrower PDI and a lower  $M_w$ . **Poly1** was also reacted with excess phenylacetylene **3** to afford **poly2** (Scheme 2) with  $M_w$  of 15 700 and PDI of 2.1. A low molecular mass model compound (**5**) was prepared starting from diiodoarene **2** and BODIPY **4**.

#### 3.2. Structure characterization

The  $^1\text{H}$  NMR spectra of **poly1** and **poly3** in  $d$ -chloroform are displayed in Fig. 1. At first glance, the spectra of **poly1** and **poly3** look very similar. However, there are some new small signals at 2.4 ppm (methyl of *p*-tolyl), 5.3 ppm (benzylic H of **4**), 6.1 ppm (pyrrole H of **4**) and above 7.3 ppm (pyridine H), which indicate that BODIPY **4** has been connected to **poly1**.

The  $^1\text{H}$  NMR spectrum was also used to determine the BODIPY content in **poly3**. GPC analysis shows that  $M_w$  and  $M_n$  of **poly3** are 13.3 and 10.3 kDa, respectively, indicating the degree of polymerization is about 19 (not including the end groups). Thus, each **poly3** is estimated to be end-capped with 1.2 BODIPY groups by the integration of the PPE  $\text{CH}_2\text{O}$  group ( $\delta$  4.01 ppm) and the picolyl  $\text{CH}_2$  ( $\delta$  5.30 ppm) signals in  $^1\text{H}$  NMR [28,29].

#### 3.3. UV–vis absorption spectra of **poly2**, **poly3**, **4** and **5**

The normalized UV–vis absorption spectra of **poly2**, **poly3** and the model compounds **4** and **5** in toluene are displayed in Fig. 2. In this solvent, the absorption spectrum of **5** shows a strong and broad  $S_1 \leftarrow S_0$  ( $\pi-\pi^*$ ) transition with maximum at 567 nm, assigned to the BODIPY chromophore [30]. The shoulder at 535 nm is assigned to vibrational progression of the same electronic transition. A second more energetic transition with maximum at 390 nm is attributed to

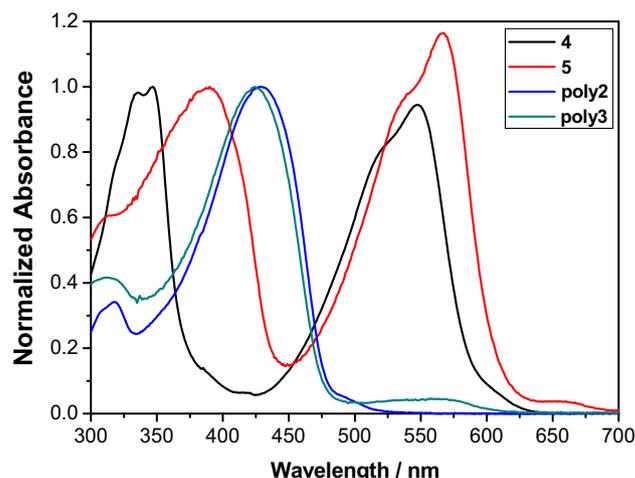
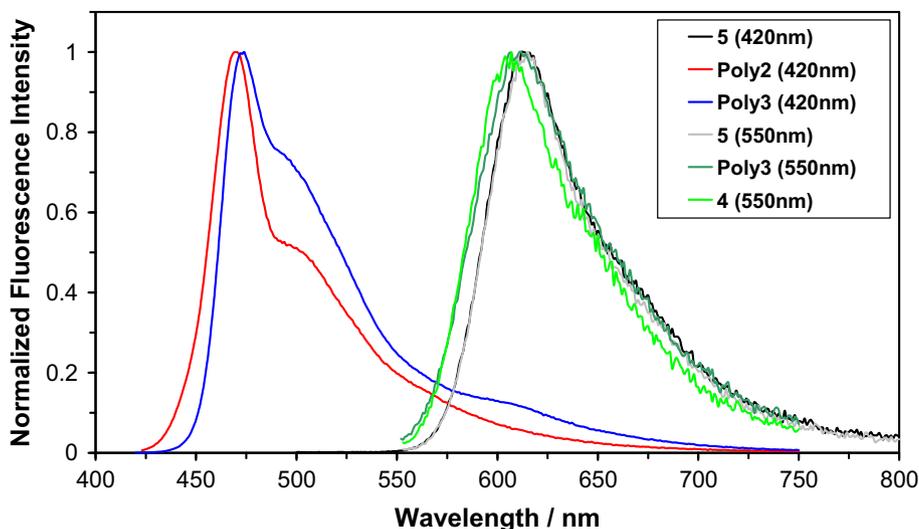


Fig. 2. Normalized UV–vis absorption spectra of **4**, **5**, **poly2** and **poly3** in toluene. The spectra of **5**, **poly2** and **poly3** are normalized at the maximum of absorption band of the *p*-phenylene ethynylene linker. The spectrum of **4** is normalized at the maximum of the UV absorption band.



**Fig 3.** Normalized fluorescence emission spectra in toluene solution of **poly2**, **poly3** and **5** upon excitation at 420 nm and of **poly3**, **4** and **5** with  $\lambda_{\text{ex}} = 550$  nm. The  $\lambda_{\text{ex}}$  values used are given in parentheses. All the spectra are normalized at the maximum of the emission band.

the  $\pi-\pi^*$  transition of the *p*-phenylene ethynylene linker [31]. The weak and broad absorption band attributed to the  $S_n \leftarrow S_0$  transition of BODIPY is not observed because it is hidden under the much stronger transition of the *p*-phenylene ethynylene substituent [30]. The long wavelength part of the absorption spectrum of **5** corresponds, except for a red shift, to that of model compound **4**. **Poly2** shows a very strong absorption peak at 429 nm, assigned to the  $\pi-\pi^*$  transition of poly(*p*-phenylene ethynylene) [32] and has no absorption after 510 nm. The UV–vis absorption spectrum of a dilute toluene solution of **poly3** displays an intense absorption centered at 424 nm as well as a much weaker absorption with a maximum around 555 nm assigned to the BODIPY-based terminal groups, which further confirms that BOIPY has been successfully connected to **poly1**.

Similar absorption spectra of **poly2**, **poly3**, **4** and **5** were measured in THF. In this solvent, the maxima of **poly2** and **poly3** were found at 427 and 423 nm, respectively, while the maximum of **5** corresponding to the  $S_1 \leftarrow S_0$  transition was observed at 556 nm with a shoulder at 526 nm and the maximum of the  $S_n \leftarrow S_0$  transition at 390 nm. The spectral maxima of **4** were blue-shifted compared to those of **5**:  $S_1 \leftarrow S_0$  transition at 547 nm and  $S_n \leftarrow S_0$  transition at 347 nm.

#### 3.4. Fluorescence emission properties of **poly2**, **poly3**, **4** and **5**

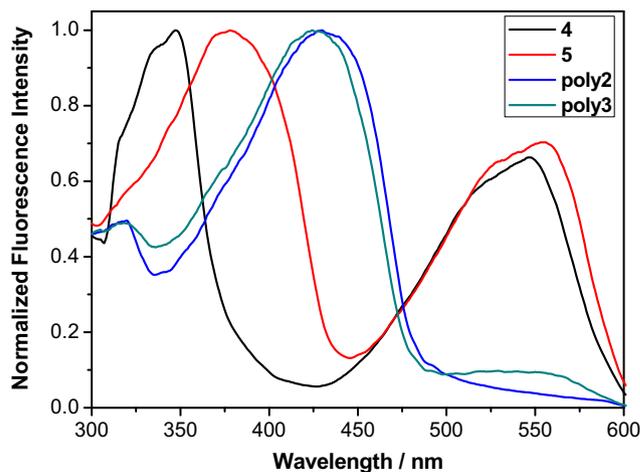
The steady-state fluorescence emission spectra of **poly2**, **poly3**, **4** and **5** in toluene are displayed in Fig. 3. Upon excitation at  $\lambda_{\text{ex}} = 420$  nm, **poly2** shows an emission peak at 470 nm and a shoulder at 503 nm due to a coupling of the phenylene ring stretching modes of the main chain to the electronic transitions between  $\pi$  and  $\pi^*$  states [32]. Excitation of **poly3** at the same wavelength (420 nm) gives a main emission peak at 474 nm, a shoulder at 498 nm, and a weak emission peak at 613 nm, which can be assigned to the BODIPY moiety. Comparing the emission spectra of **poly2** and **poly3** suggests that at 613 nm about 50% of the emission is due to the BODIPY chromophore. Because at 420 nm the absorption of the BODIPY chromophore will be negligible (see excitation spectrum of **4** in Fig. 4) compared to that of the linker, this indicates that excitation transfer occurs.

The fluorescence quantum yield  $\Phi_f$  upon excitation at 420 nm of **poly3** in toluene equals 0.53, which is similar to that of **poly2** ( $\Phi_f = 0.54$ ) under the same conditions.

Upon excitation (of the BODIPY chromophore) at 550 nm, **poly3** and **4** show emission spectra in toluene with maxima at 612 nm and 607 nm, respectively. The long wavelength part of the fluorescence emission spectrum of **5** is independent of the excitation wavelength ( $\lambda_{\text{ex}} = 420$  nm and 550 nm: grey and black curves in Fig. 3). Upon excitation at 550 nm, the measured  $\Phi_f$  values of **poly3**, **4** and **5** in toluene amount to 0.18, 0.11 and 0.14, respectively. These values are comparable to those of other 3-amino substituted BODIPYs [30].

The emission spectra of **poly2**, **poly3**, **4** and **5** in THF are very similar to those obtained in toluene under the same conditions. Upon 420 nm excitation, the fluorescence quantum yields of **poly2** and **poly3** in THF equal 0.63 and 0.52, respectively. For **poly3**, **4** and **5** in THF, the  $\Phi_f$  values obtained upon 550 nm excitation are 0.14, 0.10 and 0.10, respectively.

The long wavelength band found in the excitation spectrum of **4** is characteristic for the BODIPY chromophore. The excitation spectrum of **5** consists besides a long wavelength band characteristic for absorption by the BODIPY chromophore of a second band of similar intensity which coincides with the absorption band attributed to the linker. The relative intensities of both bands are quite similar to those in the absorption spectrum which suggests energy



**Fig 4.** Normalized fluorescence excitation spectra of **4**, **5**, **poly2** and **poly3** in toluene at room temperature observed at 615 nm. All the spectra are normalized at the maximum of the main excitation band ( $<450$  nm).

transfer with nearly 100% efficiency. The excitation spectrum of **poly3** consists of a long wavelength band corresponding to that found in **4** and **5** and an extra band with a maximum around 430 nm. The latter band which is also observed in the excitation spectrum of **poly2** corresponds to the absorption bands of the poly (*p*-phenylene ethynylene) linker in **poly2** and **poly3**. From the emission spectrum it is clear that the emission of **poly3** at 613 nm is only for 50% due to the linker. Furthermore, the maximum of the band at 474 nm is about ten times more intense than that due to the BODIPY chromophore. This means that in the excitation spectrum of the emission of the BODIPY chromophore the band due to the linker is five times more intense than that of the BODIPY chromophore while in the absorption spectrum it is about twenty times more intense. The limited excitation transfer in **poly3** comes as no surprise because the edge to edge distance of chromophores in the center of the PPE linker to the BODIPY is more than 10 nm in **poly3**, a value clearly exceeding generally accepted values for the Förster distance (4–6 nm) for completely allowed transitions [33]. This suggests that changing the conditions of the polymerization in order to reduce the length of the OPE linker by a factor of two would be necessary to obtain efficient energy transfer.

#### 4. Conclusion

BODIPY chromophores have been successfully introduced at the ends of PPE by a palladium-catalyzed cross-coupling reaction. The absorption and emission spectra show that linking BODIPY to the PPE linker does not perturb the spectroscopic properties of both the linker and BODIPY. The similar fluorescence quantum yields obtained upon direct excitation of the BODIPY chromophore in model compound **5** and in polymer **poly3** suggests that linking the chromophores does not induce significant quenching, e.g. by electron transfer. Although the PPE linker was shown to act as antenna in both the model compound **5** and the polymer **poly3**, excitation transfer only occurs with limited yield in **poly3**.

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