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# Optical Spectroscopy of Grafted Poly(*p*-phenyleneethynylene)s in Water and Water−DMF Mixtures

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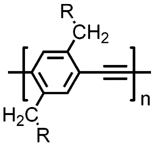
ABSTRACT: The synthesis and spectral characterization of three grafted poly(*p*-phenyleneethynylene)s (PPE) are reported. These polymers contain identical chromophores/fluorophores yet show different absorption and emission spectra in DMF and DMF−water mixtures. While some of the spectral properties of the PPEs are similar to those of didodecyl-PPE, their spectroscopic properties in DMF−water mixtures differ significantly from those of didodecyl-PPE in $CHCl_3$. An example is the lactide-substituted PPE, which shows absorption spectra that are reminiscent of those obtained for didodecyl-PPE in poor solvents but emission spectra that resemble those of didodecyl-PPE in a good solvent. Emission shifts occur in these PPEs when going from DMF to water. In the case of the lactide-PPE, a surprising hypsochromic emission shift of 10 nm is observed. This apparent shift is attributed to the preferred aggregation and self-quenching of the longer chains, leaving shorter, blue-emissive chains nonaggregated.

## Introduction

Conjugated polymers are popular in organic electronics[1] and sensory[2] applications due to their tunable and often strong fluorescence in solution and in the solid state.[3] Understanding electronic transitions in conjugated polymers, both absorption and emission, is complex. This is true even if the polymer under consideration is dissolved at very low concentration in a good solvent where aggregation, agglomeration (i.e., mechanical association of polymer chains without significant electronic ground-state interaction of the chains), and excimer formation can be excluded. An important example is the rotational invariance in the ground-state and excited-state planarization of large phenyleneethynylene oligomers and polymers, which accounts for their narrow fluorescence and their broad absorption.[4]

Poly(*p*-phenyleneethynylene)s (PPE), the dehydrogenated congeners of the poly(*p*-phenylenevinylene)s (PPV), display, despite their apparent similarity, differing optical and electronic properties. Rotational invariance in the ground state (in solution) and quadratic coupling in the excited state combined with the electron-accepting nature of the triple bond determine the spectroscopic behavior of PPEs both in thin films and in solution. We and others have investigated PPEs and attributed their absorption and emission behavior to a complex interplay of intermolecular interactions and intramolecular conformational changes.[5,6] Conformational changes, i.e., planarization and deplanarization, play an important role in PPEs, even though recently the contribution of planarization to the red-shifted absorption bands of PPEs has been disputed by Leclerc.[6a] Berg and Yaron, however, developed a configuration-coordinate model, *supporting* the presence of strong torsional effects that dominate the electronic transitions of the PPEs in absorption and in emission.[7]

In this contribution we describe the influence of different polymeric side chains on the optical behavior of "dialkyl"-PPEs in polar solvents and water. The three investigated polymers have the backbone of a dialkyl-PPE, yet their solvent-dependent spectroscopic properties are significantly modified. When comparing their UV−vis and emission spectra in water, the spectroscopic properties of the main chain can be manipulated to a surprising extent by the proper choice of side chain. This investigation bears influence on and constitutes a road map toward the selection and use of PPE types for potential sensory and organic electronics applications.


Dialkyl-PPE

## Results and Discussion

**Synthesis and Characterization.** The syntheses of the polymers **4**, **9**, and **11** are straightforward and shown in Schemes 1−3. For the synthesis of **4** and **9** the macromonomers **3** and **8** are produced by a ring-opening polymerization of either **2** or **6** with 3,6-dimethyl-1,4-dioxane-2,5-dione and 2-methyloxazoline, respectively. The macromonomers **3** and **8** were reacted with acetylene gas[8] in a mixture of piperidine and THF as solvent in the presence of 0.2 mol % $(Ph_3P)_2PdCl_2$ as catalyst. In the case of **4**, the polylactide side chains survive the treatment with piperidine without appreciable ester cleavage. The degree of polymerization ($P_n$) for both **4** and **8** is around 20−30 repeat units according to gel permeation chromatography (GPC). The synthesis of the PPE **11** starts from the literature known polymer **10**, which is quantitatively quaternized by the addition of triethylamine.[9] The polymers **4** and **9** are nonionic, and the polymer **11** is highly positively charged. The three PPEs are well soluble in DMF as polar aprotic solvent, while only **9** and **11** are soluble in water. However, **4** is soluble in DMF/water mixtures that contain up to 67% (vv) water without apparent precipitation or flocculation.

**Photophysics.** Dialkyl-PPEs such as didodecyl or bisethylhexyl-PPE show a broad absorption peak at 384 nm in

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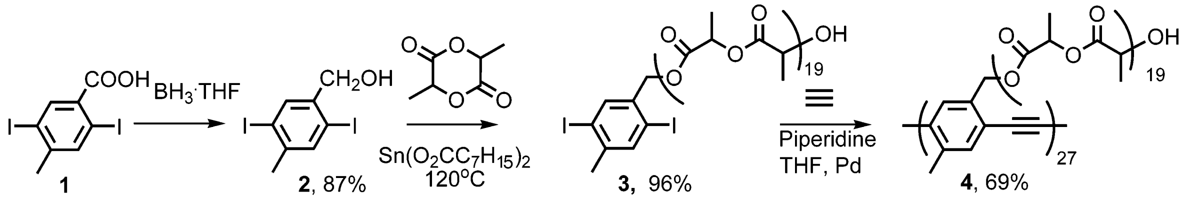
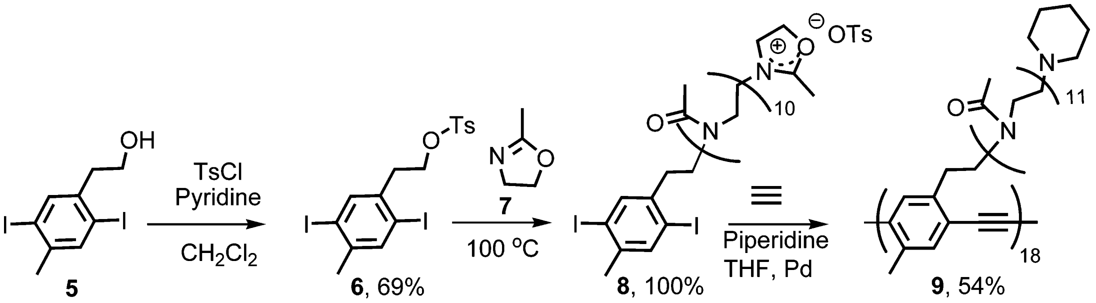
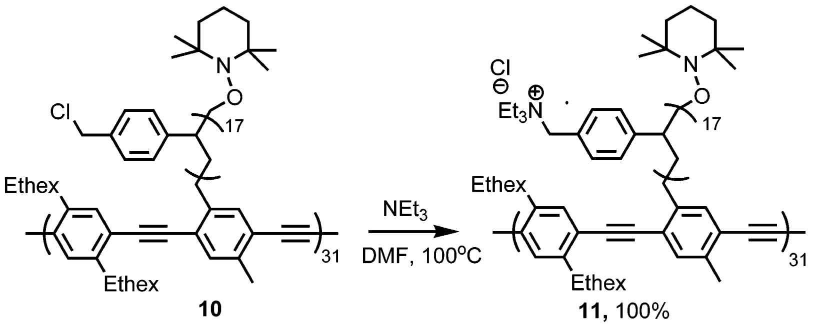
**Scheme 1. Synthesis of the Polylactide-Substituted PPE 4**



**Scheme 2. Synthesis of the Polyoxazoline-Substituted PPE 9**



**Scheme 3. Synthesis of Triethylammonium-Substituted PPE 11**



chloroform, while in the aggregated state, accessed by the addition of methanol to such solutions, a defined feature is visible at 435−440 nm. This feature is due to planarization of the conjugated main chain,[5] even though in some cases these bands were attributed to the combination of planarization and formation of electronic ground-state aggregates.[10] Emission of didodecyl-PPE in chloroform, a good solvent, is centered at 425 nm. The emission band is—surprisingly—much narrower than the absorption band.[4,5,7,11,12] The reason for the decreased spectral width in emission as compared to absorption is the planarization of the PPE chains in the excited state (quadratic coupling) and the exclusive emission from the planarized (relaxed) state.[4,5,7,12] These spectral data represent bona fide single chain events, observed in dilute solutions.

Figure 1 shows the absorption and emission spectra of **4**, **9**, and **11** in DMF, water−DMF mixtures, and water. In the case of **11**, $\lambda_{max}$(abs) is blue-shifted to 368 nm and broad, similar to that of its precursor polymer **10**. The absorption is solvent-independent, and the emission is recorded at 446 nm, i.e., red-shifted in comparison to that of dialkyl-PPEs. Upon increasing the water content, the absorption spectrum does not change, but the emission spectrum blue shifts to 428 nm, being similar to that recorded for dialkyl-PPEs, however, significantly broadened. This broadening of the absorption and the emission of **11** is probably due to the enforced deplanarization or twist of neighboring phenyleneethynylene units carrying charged and bulky polystyrene side chains. Despite the twist, however, the emission is red-shifted and the emissive lifetime increased from 0.4 ns (didodecyl-PPE) to 1.1 ns (**11**, Tables 1 and 2). We interpret this behavior as a consequence of the formation of loose excimers in the twisted rods of **11** in DMF. As water is a better solvent for this polyelectrolyte, these excimers are in equilibrium with their respective monomeric chains, hence the observed blue shift in emission.

The spectroscopic properties of **4** in DMF and in mixtures of water−DMF resemble those observed for didodecyl-PPE (Figure 1). The absorption spectrum of **4** in DMF displays a main band at 403 nm and a shoulder at 437 nm (Table 1). The spectral features suggest that a partially planarized structure, a structure with a decreased torsion angle, or mixtures of planarized and nonplanarized PPE chains are present in DMF. Upon the addition of water, planarization by chain agglomeration sets in, and the feature at 437 nm becomes the most prominent one. Upon increasing the solvent polarity we find that the emission maximum *blue* shifts from 425 to 414 nm (41% water). Upon further addition of water, the emission at 414 nm disappears completely and gives rise to the excimer-type emission of PPEs recorded at 512 nm. These excimer type emissions have variable emission maxima that change with concentration and solvent, ranging from 500 to 540 nm, depending upon the specific conditions. These effects have been discussed by us and others recently.[5,13]

While the UV−vis spectrum of **4** in DMF shows only a small contribution from the planarized form, i.e., a shoulder at 437 nm, after the addition of 17% water the chains of **4** are fully planarized as the band at 437 nm is now the main feature (Figure 2). The corresponding emission spectra, however, resemble those of didodecyl-PPE in a good solvent such as chloroform, strongly underscoring that these polymeric materials *are* dialkyl-PPEs. A puzzling obervation was the apparent negative Stokes shift

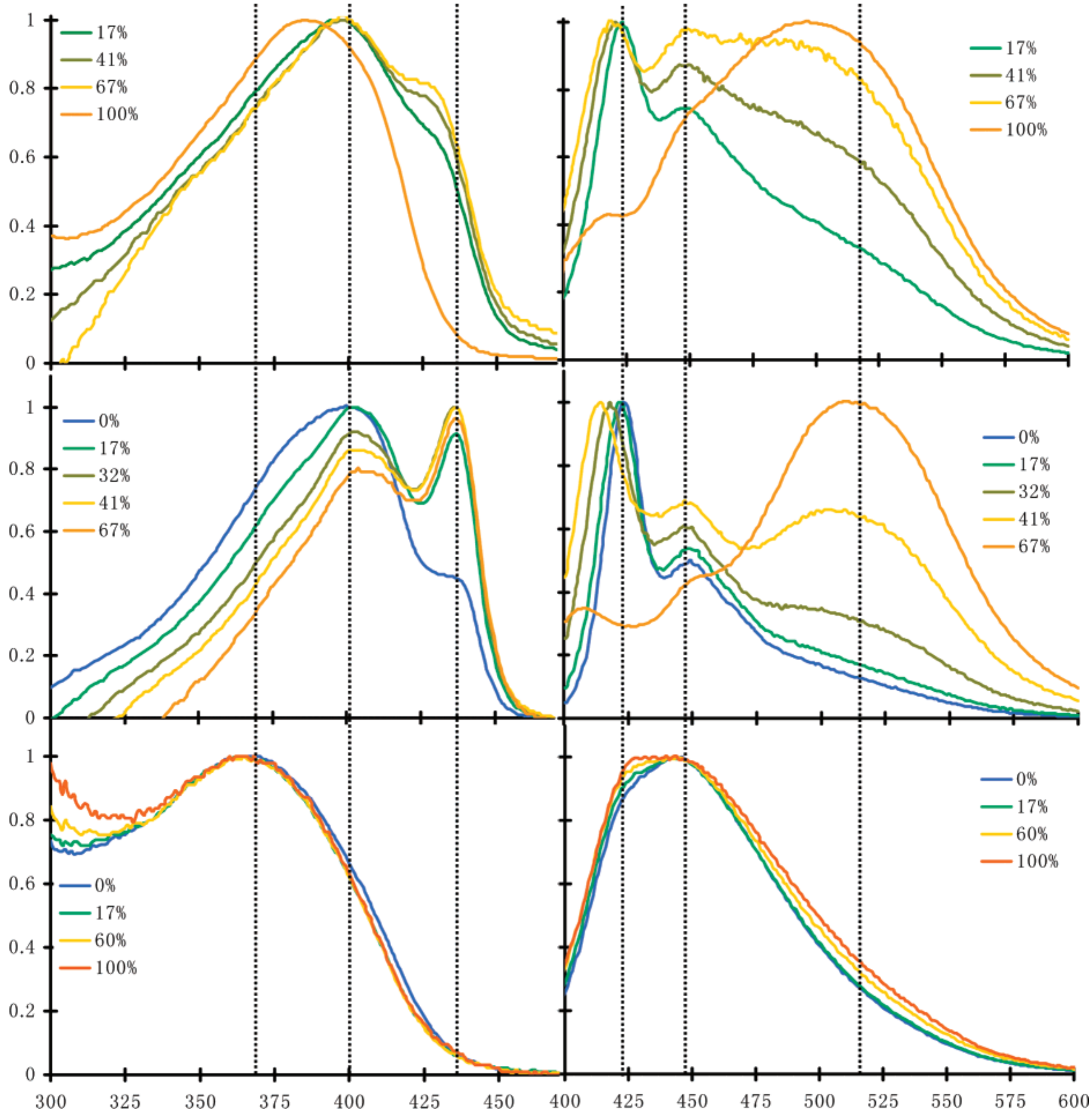


**Figure 1.** Normalized spectral features of **9** (top), **4** (middle), and **11** (bottom) in absorption and emission in DMF and water and in mixtures of both. Numbers represent the percent of added water to DMF solutions of the polymers. The emission spectra were obtained at an excitation of 400 nm.

**Table 1. Absorption and Emission Spectra (nm) of the Polymers 4, 9, and 11**

| | 0% $H_2O$ | | 17% $H_2O$ | | 32% $H_2O$ | | 41% $H_2O$ | | 60% $H_2O$ | | 67% $H_2O$ | | 100% $H_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | abs | em | abs | em | abs | em | abs | em | abs | em | abs | em | abs | em |
| **4** | 403 | 425 | 437 | 422 | 437 | 418 | 437 | 414 | na | na | 437 | 512 | na | na |
| **9** | na | na | 396 | 419 | na | na | 426 | 421 | na | na | 427 | 419 | 386 | 498 |
| **11** | 368 | 446 | 368 | 446 | na | na | na | na | 368 | 428 | na | na | 368 | 428 |

of the emission band located at 414 nm in a 40/60 mixture of DMF/water. Performing excitation spectroscopy at 420, 450, and 500 nm of a solution that contained **4** in 0, 10, 20, 30, 40, 50, and 60% water/DMF mixtures solved this puzzle.[14] The excitation spectra obtained at a wavelength of 500 nm did not show any dependence upon the water content of the solvent and were superimposable to the UV−vis spectrum in which the planarization band is prominent. However, if the excitation spectrum was recorded at 420 nm, the maximum of the excitation spectrum changed significantly with the solvent composition. In DMF the maximum of the excitiation spectrum was recorded at 405 nm, while in 60/40 water/DMF the maximum of the excitation spectrum was shifted to 361 nm.

The blue shift in the fluorescence of **4** and to a lesser extent in **9** upon addition of water to their solutions in DMF can be understood if we assume that preferred aggregation/agglomeration occurs for the longer chain PPEs, while the PPEs with lower molecular weight stay unaggregated under these conditions.[15] As a consequence, the high molecular weight fractions of **4** or **9** form excimeric species that emit at 510 nm, while the lower molecular weight fractions of **4** (or **9**) under the same conditions are unaggregated or unagglomerated and emit at their innate emission wavelength.

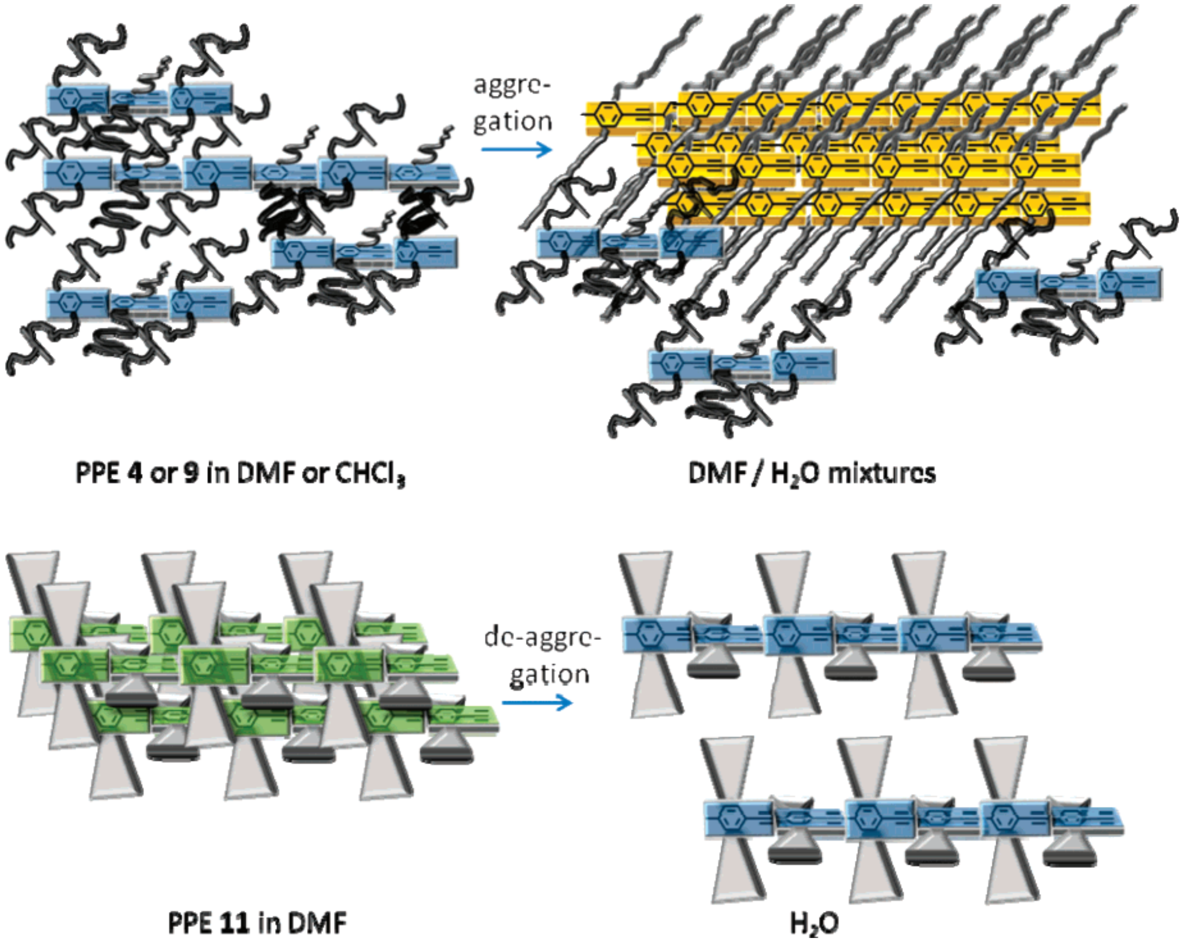


**Figure 2.** Interplay of aggregation and planarization of the PPEs **4**, **9**, and **11** in DMF and in water. The chosen colors represent the approximate emission colors. In the top panel the larger polymer chains are shown to agglomerate and become less fluorescent while the smaller ones stay unaggregated and are responsible for the observed blue-shifted fluorescence upon addition of water.

**Table 2. Emissive Lifetimes (ns) of the Polymers 4, 9, and 11 in Different Solvents**

| | $CHCl_3$ | | DMF | | $DMF/H_2O$ (80:20) | | $H_2O$ | |
|---|---|---|---|---|---|---|---|---|
| | $\tau_{420\ nm}$ | $\tau_{460\ nm}$ | $\tau_{420\ nm}$ | $\tau_{460\ nm}$ | $\tau_{420\ nm}$ | $\tau_{460\ nm}$ | $\tau_{420\ nm}$ | $\tau_{460\ nm}$ |
| **4** | 0.42 | 0.43 | 0.46 | 0.48 | 0.69 | 0.81 | na | na |
| **9** | 0.39 | 0.40 | 0.67 | 0.77 | na | na | 0.86 | 0.91 |
| **11** | 0.37 | 0.45 | 0.37 | 0.45 | na | na | 0.62 | 1.1 |

The UV−vis spectra of **9** in mixtures of DMF−water show a $\lambda_{max}$ at 400 nm, with a shoulder at 426 nm that increases upon increasing water content. However, in pure water a broad absorption feature with a $\lambda_{max}$ of 386 nm is observed. The emission of **9** in DMF is centered at 419 nm. In water, the main chains of **9** are twisted, probably due to the full hydration of the hydrophilic side chains. The PPE **9** shows a $\lambda_{max}$ emission in water at 498 nm, suggesting the presence of excimeric contributions despite the presence of a twisted chain geometry. An increase in emissive lifetime to 0.9 ns (Table 2) is also indicative of the formation of excimers. In the case of **9** changes in the absorption spectrum are concomitant to changes in the emission spectra.

We have investigated the emissive lifetimes of the three PPEs in different solvent mixtures. The lifetime of the emission at 420 nm (chloroform) is around 0.4 ns for **4**, **9**, and **11** (DMF), in agreement with literature values[13] and quite typical for dialkyl-PPEs (Table 2). In good solvents, the emission at 460 nm shows the same lifetime, asserting that both emissions emanate from the same state. Upon going to DMF−water mixtures the emission lifetimes of all polymers increase to ∼1 ns. In the case of **11** (water) the emissive lifetime of the feature at 420 nm is 0.6 ns, while that recorded at 460 nm is 1.1 ns. The two emissions therefore probably originate from different species. The data suggest that the feature observed at 420 nm (0.6 ns) comes from the monomeric chains, while the emission recorded at 460 nm is due to an excimeric species. Despite their different line shape and line widths, however, the emissions of all the three PPEs **4**, **9**, and **11** in DMF show identical emissive lifetimes.

## Conclusions

In conclusion, we have investigated the solvatochromic properties arising in DMF/water mixtures of three differently grafted PPEs. The benzene rings in these PPEs carry alkyl-type substituents and are therefore by definition electronically identical to dihexyl- or didodecyl-PPE. Yet by selecting different polymeric side chains, the absorption and emission maxima and the spectral shapes of absorption and emission are significantly shifted, depending upon the chemical environment the PPE backbones are exposed to. Dialkyl-PPEs have potential as environmentally sensitive emitters in solution and in the solid state, transmitting environmental parameters by change of absorption and/or emission color.[16]

## Experimental Part

**Characterization.** The $^1H$ and $^{13}C$ NMR were measured on a Varian 300 MHz spectrometer or on a Bruker 400 MHz spectrometer using a broadband probe. IR data were collected by a FTIR-8400S infrared spectrophotometer (Shimadzu). The emission spectra were taken by RF-5301 PC spectrofluorophotometer (Shimadzu). GPC measurements were conducted in chloroform (25 °C) with a SCL-10A VP UV−vis detector (Shimadzu). The molecular weights were determined versus polystyrene standards. All of the obtained PPEs were dried under oil pump vacuum at temperatures around 60−80 °C and redissolved easily after the drying procedure in common organic solvents.

**Quantum Yields.** All absorption spectra were collected using a Shimadzu UV-2401PC spectrophotometer. All emission spectra were acquired using a Shimadzu RF-5301PC spectrofluorophotometer. The fluorescence quantum yields were determined with reference to quinine sulfate ($10^{-6}$ M in 0.1 M $H_2SO_4$, $\Phi = 0.54$, all solutions were purged with nitrogen prior to measurement) using standard procedures according to ref 14.

**Compound 1**. To a nitrogen-purged flask were added 2,5-diiodo-4-methylbenzoic acid (7.76 g, 20.0 mmol) and dry THF (50 mL), stirred under nitrogen at 0 °C until the acid dissolved. $BH_3$·THF (1.0 M in THF) (30 mL, 30.0 mmol) was added slowly. The solution was stirred at 0 °C for 30 min and at room temperature for another 24 h. The excess $BH_3$ was quenched by ice water (500 mL), and a colorless precipitate formed. The crude product was redissolved in ether and further purified by a silica gel column to give (2,5-diiodo-4-methylphenyl)methanol as a colorless solid (6.50 g, 87%). IR (KBr) $cm^{-1}$ = 3351, 3207, 2970, 1695; mp = 186−187 °C. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta = 7.78$ (s, 1H), 7.73 (s, 1H), 4.30 (s, 2H), 2.29 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta = 143.1$, 142.2, 139.9, 138.2, 102.0, 97.3, 68.5, 27.1. Anal. Calcd for $C_8H_8I_2O$: C 25.69, H 2.16. Found: 25.53, 2.16.

**Macromonomer 3**. An oven-dried Schlenk flask, cooled under nitrogen, was charged with (2,5-diiodo-4-methylphenyl)methanol (1.87 g, 5.00 mmol), 3,6-dimethyl-1,4-dioxane-2,5-dione (7.20 g, 50.0 mmol), and tin(II) 2-ethylhexanoate (127 mg, 313 $\mu$mol). The flask was heated while stirring to 120 °C. The reaction was stopped after 12 h. The light yellow solid product was diluted with chloroform (10 mL) and then precipitated into ether (300 mL). The diiodo-polyester **3** was obtained as a colorless solid (8.76 g, 96%). GPC (vs polystyrene standards in chloroform): $M_n = 1.8 \times 10^3$, $M_w/M_n = 1.24$. $P_n = 19$. IR (KBr) $cm^{-1}$ = 3489, 2986, 2613, 2379, 2048, 1751, 1448. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta = 7.70$ (s, 1H), 7.60 (s, 1H), 5.30−4.98 (b, 21H), 4.20−4.40 (b, 1H), 2.30 (s, 3H), 1.70−1.30 (m, 60H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta = 169.7$, 169.5, 169.5, 169.2, 144.1, 140.1, 139.6, 136.8, 100.9, 98.1, 72.7, 70.0, 69.5, 69.3, 66.7, 27.6, 20.8, 17.3, 17.1, 17.0, 16.5, 16.2.

**Polymer 4**.[15] The diiodo polyester **3** (2.56 g, 1.40 mmol) was combined with piperidine (1.5 mL), THF (1.5 mL), $(PPh_3)_2PdCl_2$ (2.0 mg, 2.8 $\mu$mol, 0.2 mol %), and CuI (1.0 mg, 5.3 $\mu$mol, 0.4 mol %) in a Schlenk flask of known volume (37 mL). Acetylene gas (34 mL, 1.4 mmol) was added through the side arm with a balloon. The reaction was allowed to stir at room temperature for 24 h. The resulting polymer, **4**, was filtered over a cotton plug using dichloromethane as a solvent before precipitating into ethyl ether. The polymer **4** was collected over a fritted funnel, redissolved in dichloromethane, and precipitated in hexane again. A bright yellow polymer was obtained (1.56 g, 69% yield). GPC (vs polystyrene standard in chloroform): $M_n = 49 \times 10^3$, $M_w/M_n = 3.7$. Repeat = 1800 g/mol, $P_n = 27$. IR (KBr) $cm^{-1}$ = 3479, 2987, 2157, 1740, 1734. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta = 7.40$−7.25 (bd, 2H), 5.30−4.98 (b, 21H), 4.20−4.40 (b, 1H), 2.30 (bs, 3H), 1.70−1.30 (m, 60H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta = 175.0$, 170.6, 169.5, 169.3, 169.0, 140.4, 138.5, 135.0, 123.9, 123.2, 93.5, 92.7, 69.3, 69.1, 68.9, 66.6, 65.0, 29.6, 27.6, 20.9, 19.9, 16.6, 16.5. Quantum yield $\Phi = 0.81$ ($CHCl_3$). Quantum yield $\Phi = 0.31$ (DMF).

**Compound 6.** An oven-dried Schlenk flask, cooled under nitrogen, was charged with 2,5-diiodo-4-methylphenethyl alcohol **5** (2.00 g, 5.03 mmol), *p*-toluenesulfonyl chloride (1.07 g, 5.53 mmol), pyridine (1.0 mL), and chloroform (30 mL). The reaction was magnetically stirred at room temperature for 12 h. The reaction mixture was washed twice with water (50 mL). A colorless solid was collected after the solvent was removed in vacuo. The crude product was further purified by crystallization from methanol to give **6** (1.93 g, 69%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta = 7.67$ (d, 2H), 7.55 (s, 1H), 7.50 (s, 1H), 7.26 (d, 2H), 4.20 (t, Hz, 2H), 4.05 (t, $J_{3H,H} = 6.8$ Hz, 38H), 2.42 (s, 3H), 2.32 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta = 144.8$, 142.4, 140.2, 134.0, 138.1, 132.9, 129.9, 128.0, 101.1, 99. 9, 68.9, 39.1, 27.4, 22.1.

**Macromonomer 8**. To a nitrogen-purged flask, tosylate **6** (0.771 g, 1.40 mmol) and 2-methyl-2-oxazoline **7** (1.19 g, 14.0 mmol) were added. The flask was heated while stirring to 105 °C. The reaction mixture solidified after 1 h. The excess monomer was removed in high vacuum at 100 °C to give spectroscopically pure **8** (1.96 g, 100%). IR (KBr) $cm^{-1}$ = 3024, 1741, 1641, 1616, 1574. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta = 7.69$ (bs, H), 7.60 (bs, H), 7.59−7.56 (b, 2H), 7.19−7.15 (b, 2H), 3.77−3.70 (b, 2H), 3.60−3.30 (b, 40H), 2.38−2.32 (b, 6H), 2.22−1.98 (b, 30H) $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta = 170.7$, 169.8, 144.8, 142.3, 139.7, 138.2, 129.9, 128.89, 127.9, 125.8, 101.0, 99.9, 69.0, 47.8, 47.1, 45.5, 44.0, 39.0, 27.3, 22.0, 21.5. GPC (vs polystyrene standard in chloroform): $M_n = 1.3 \times 10^3$, $M_w/M_n = 1.2$.

**Polymer 9**. The diiodomonomer **8** (1.85 g, 1.41 mmol) was combined with piperidine (1.5 mL), methanol (1.5 mL), $(PPh_3)_2PdCl_2$ (2.0 mg, 2.8 $\mu$mol, 0.2 mol %), and CuI (1.0 mg, 5.3 $\mu$mol, 0.4 mol %) in a Schlenk flask (37 mL). Acetylene gas (34 mL, 1.4 mmol) was added through the purged side arm with a balloon. The reaction was allowed to stir at room temperature for 24 h. The resulting polymer **9** was filtered over a cotton plug using dichloromethane as a solvent before precipitating into THF; **9** was collected over a fritted funnel, redissolved in dichloromethane, and precipitated in ethyl ether to give **9** as yellow polymer (0.831 g, 54% yield). GPC (vs polystyrene standard in chloroform): $M_n = 23 \times 10^3$. Repeat = 1300 g/mol, $P_n = 18$, $M_w/M_n = 3.7$. $^1H$ NMR ($CDCl_3$, 400 MHz): 7.41 (bs), 4.36 (bs, 2H), 4.04 (bt, $J_{3H,H} = 6.6$ Hz, 38H), 3.62 (bs, 2H), 2.94 (bs, 2H), 2.28 (bt, $J_{3H,H} = 7.4$ Hz, 40H), 1.62 (bm, 80H), 1.36 (bm, 40H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 173.8$, 173.5, 138.3, 136.7, 133.4, 132.8, 123.9, 123.2, 93.2, 92.5, 65.2, 64.1, 63.1, 62.6, 34.1, 32.3, 28.3, 25.5, 25.3, 24.5, 20.3. IR (KBr) $cm^{-1}$ = 3567, 3268, 2967, 1669, 1631, 1474. Quantum Yield: $\Phi = 0.28$ (DMF), $\Phi = 0.66$ (chloroform), $\Phi = 0.12$ (water).

**Polymer 11**. To a 50 mL nitrogen-purged round-bottom flask, **10**[9] (100 mg, 100 $\mu$mol), triethylamine (1.01 g, 10.0 mmol), and DMF (5 mL) were added. The flask was heated to 100 °C overnight. The residual trimethylamine and DMF were removed in high vacuum at 100 °C. A light green polymer, **11**, was obtained in quantitative yield (112 mg, 100%). $^1H$ NMR ($CDCl_3$, 100 MHz): $\delta = 7.30$−6.90 (b), 6.80−6.30 (b), 4.40−4.00 (bs), 3.20−2.55 (bm), 1.60−0.40 (bm). Quantum yield, $\Phi = 0.19$ (water). Quantum yield, $\Phi = 0.21$ (DMF). IR (KBr) $cm^{-1}$ = 3025, 2988, 2848, 1909, 1610, 1507. Anal. Calcd for $[C_{299}H_{471}Cl_{17}N_{18}O]_n$: C, 72.74; H, 9.62; Cl, 12.21; N, 5.11; O, 0.32. Found: C: 73.21; H: 9.44.

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**Supporting Information Available:** GPC traces of **4** and **9** and UV−vis spectrum of **4** in a 95:5 ratio of DMF/water. This material is available free of charge via the Internet at http://pubs.acs.org.

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