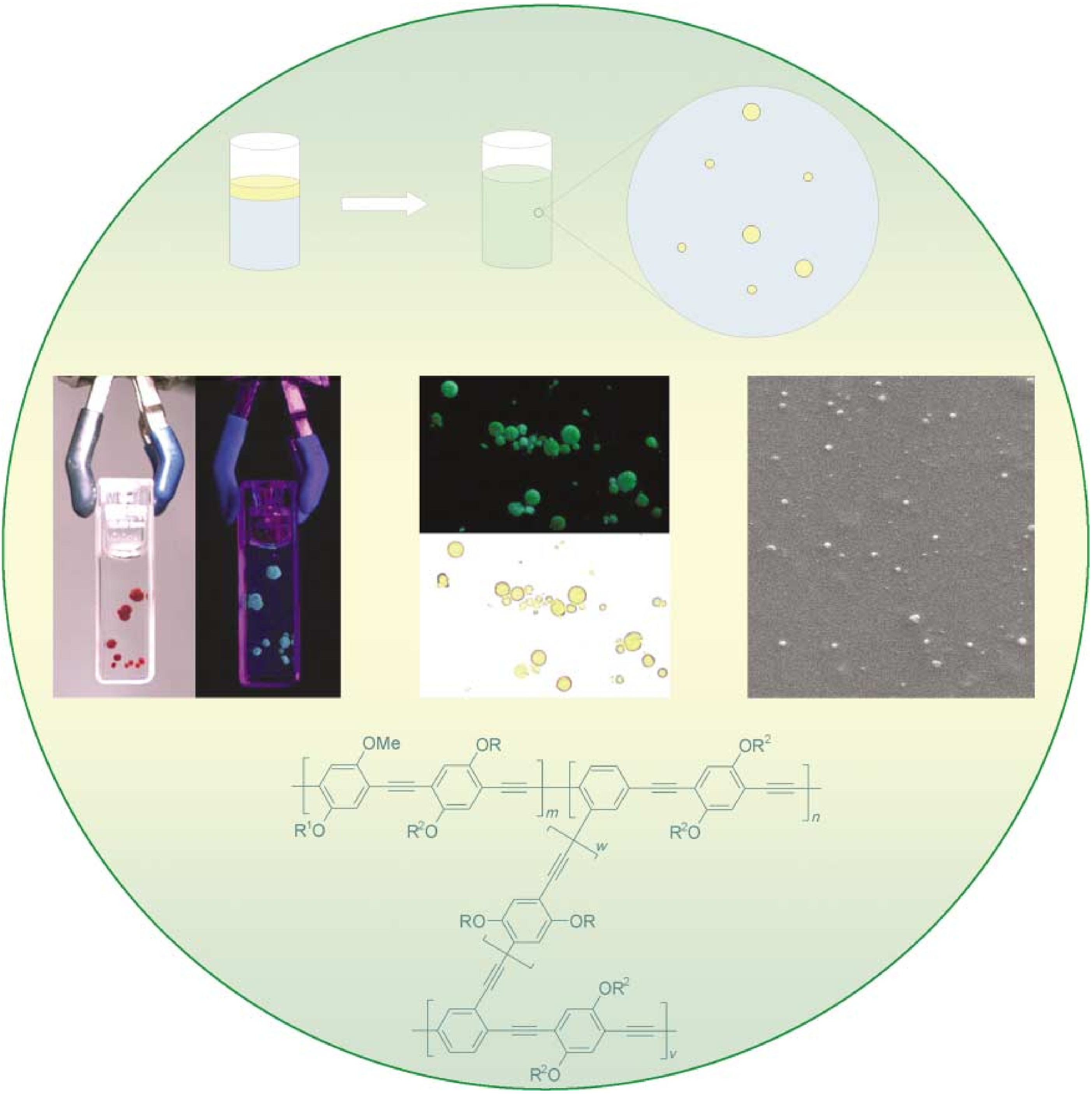
Zuschriften



Vernetzte konjugierte Milli-, Mikro- und Nanopolymerpartikel können durch Kreuzkupplungspolymerisation in wässrigen Emulsionen hergestellt werden. Über diese Materialien mit interessanten elektronischen Eigenschaften berichten C. Weder et al. in ihrer Zuschrift auf den folgenden Seiten.

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Polymer Nanoparticles

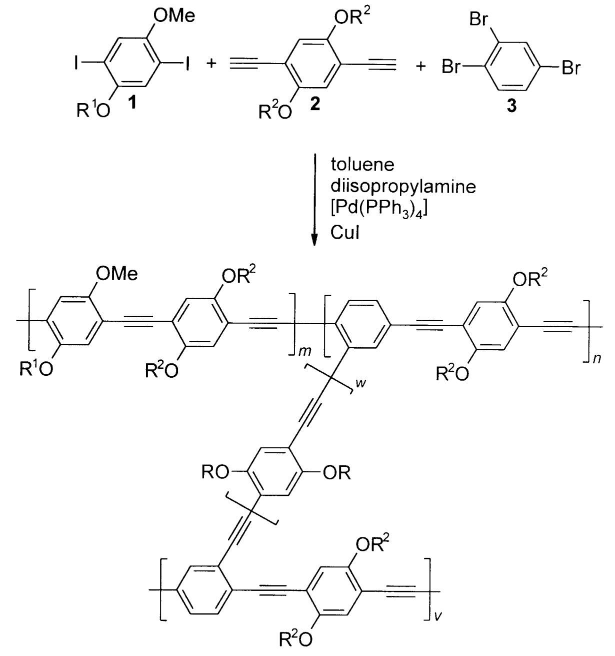
Synthesis and Characterization of Cross-Linked Conjugated Polymer Milli-, Micro-, and Nanoparticles**

*Eric Hittinger, Akshay Kokil, and Christoph Weder**

Conjugated semiconducting polymers are attracting significant interest, as these materials may combine the processability and mechanical properties of polymers with the readily tailored optoelectronic properties of organic molecules.[1] The development of conjugated polymers with unique property profiles has been propelled by their (potential) use in light-emitting diodes,[2] field-effect transistors,[3] photovoltaic cells,[4] and other devices. Our group has recently embarked on the exploration of well-defined conjugated polymer networks.[5–7] Our initial studies focused on organometallic polymers based on linear conjugated macromolecules and metallic cross-links.[5–7] We demonstrated that such networks exhibit substantially better charge-transport characteristics than amorphous films of the linear parent polymers[6] and may overcome the problems associated with interchain charge transfer between individual macromolecules.[8]

Extending the scope of this general approach, we herein report the synthesis of conjugated polymer networks comprising covalent conjugated cross-links. Interestingly, materials with this structural motif have hitherto received little attention,[9] possibly because of the difficulty of introducing conjugated cross-links and retaining adequate processability. We show here that this problem can be overcome by synthesizing such polymers in the form of spherical particles, which can be processed from (aqueous) dispersions. Applying concepts employed for the preparation of dispersions of linear conjugated polymers[10–12] and exploiting the fact that some metal-catalyzed cross-coupling reactions are tolerant to the presence of water,[13] we demonstrate that cross-linked conjugated polymer particles can be conveniently produced by polymerization in aqueous macro-, micro-, and miniemulsions. The size of the resulting particles can be readily tuned over a wide range (mm to nm) by the detailed reaction conditions, and it appears that the approach is universally applicable for many polymer systems.

The present study was based on polymers synthesized by the Pd-catalyzed cross-coupling of 2,5-diiodo-4-[(2-ethylhexyl)oxy]methoxybenzene (**1**) and 1,4-diethynyl-2,5-bis-(octyloxy)benzene (**2**; Scheme 1). The linear poly(*p*-phenylene ethynylene) (PPE) based on only **1** and **2**[14] is highly soluble and its optoelectronic properties are representative for this family of polymers.[14,15] In all experiments described herein, 1,2,4-tribromobenzene (**3**) was employed as the cross-linker. The reactivity of aryl bromides towards cross-coupling is lower than that of aryl iodides,[15] and it was expected that the reaction of **1**, **2**, and **3** would afford linear PPE segments of an appreciable length before cross-linking would lead to the gelation of the reaction mixture. While a systematic study addressing the influence of cross-linker concentration is currently underway, a stoichiometrically balanced molar ratio of about 6:9:2 of monomers **1**, **2**, and **3** was chosen here. The cross-link density should not be excessively high, as this would lead to rigid particles, which stifle adequate film formation. The reaction shown in Scheme 1 was first conducted under standard conditions,[14–16] that is, under Pd^0/Cu^I catalysis in a homogeneous toluene/iPr$_2$NH mixture (method A). Expectedly, the reaction mixture gelled after a short time and after completion of the reaction and workup the target polymer was obtained in rather large pieces. Coherent with the targeted network structure, the product could not be dissolved but swelled substantially (ca. 500% w/w) if immersed in toluene or chloroform, which are good solvents for the linear PPEs. Infrared spectra of this material, in its swollen state quite elastic, are consistent with the expected molecular structure, and elemental analysis confirms the expected composition. The analytical data reveal the presence of remaining bromine groups, thus indicating that the reaction ceases after a critical cross-link density is reached.



Scheme 1. Synthesis of cross-linked PPEs by the palladium-catalyzed cross-coupling reaction of monomers **1**, **2** and the trifunctional cross-linker **3**. R^1 = 2-ethylhexyl, R^2 = *n*-octyl.

The polymerization was repeated but conducted in a vigorously stirring mixture of water, toluene, and iPr$_2$NH (method B). Stabilized by shear forces, an "oil-in-water" emulsion was formed. Over the course of the reaction, the organic droplets adopted the characteristic color and photo-

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[*] E. Hittinger, A. Kokil, Prof. C. Weder
Department of Macromolecular Science and Engineering
Case Western Reserve University
2100 Adelbert Rd., Cleveland, OH 44106-7202 (USA)
Fax: (+1) 216-368-4202
E-mail: chw6@po.cwru.edu

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luminescence (PL) of PPEs and solidified, thus suggesting that the polymerization proceeded smoothly. The product was obtained in the form of well-separated, millimeter-sized, essentially spherical particles (Figure 1 a), which exhibited similar analytical data as the polymer produced by method A. The size of these particles may be too large to form useful suspensions, but the experiment clearly demonstrates that the Pd-catalyzed cross-coupling reaction proceeds smoothly in an aqueous emulsion.[17] In a subsequent experiment sodium dodecyl sulfate (SDS) was added as an auxiliary surfactant[11] to the otherwise unchanged reaction mixture (method C) to better stabilize the droplets and to reduce the particle size. The product was isolated as a dry powder but, as is evident from Figure 1 b, it could readily be redispersed in toluene by ultrasonication into well-separated, micrometer-sized particles without further addition of surfactant. A detailed analysis of optical micrographs of redispersed, toluene-swollen particles produced by method C shows that their size distribution is relatively narrow with an average diameter of ≈4.7 μm (Figure 2 a). The chemical composition of the polymer was comparable to the one of the materials described by methods A and B, and elemental analysis revealed that the SDS content in the final product was very low.

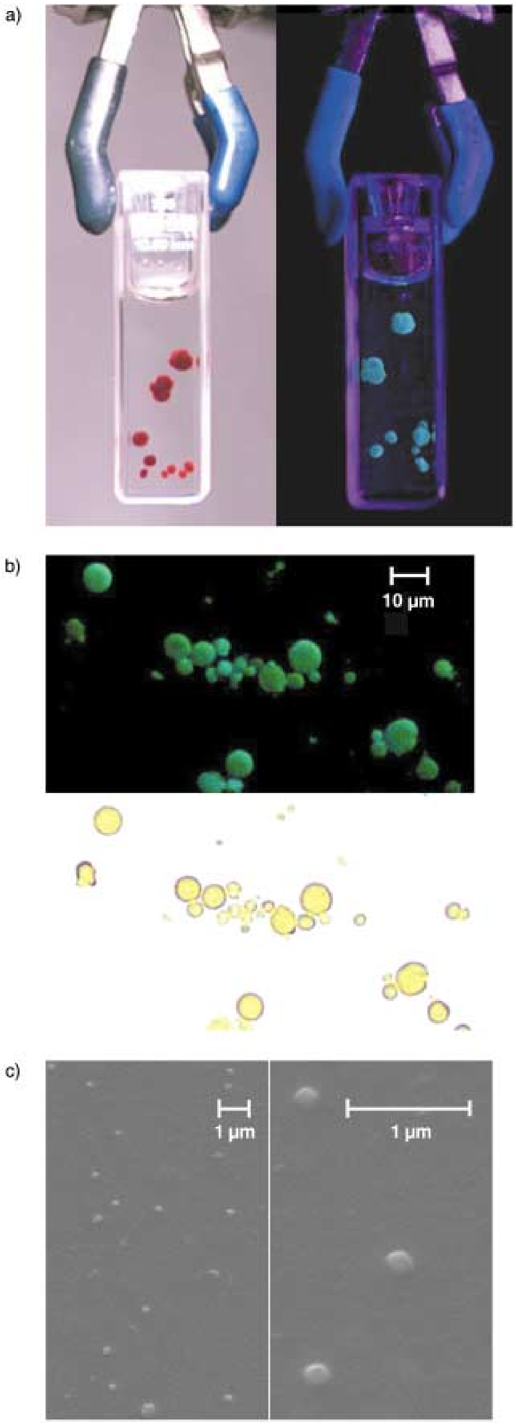

Figure 1. Photographs (a), optical micrographs (b), and scanning electron micrographs (c) of cross-linked conjugated milli- (a), micro- (b), and nanoparticles (c) prepared by method B (milli), method C (micro), and method D (nano). Pictures were taken in fluorescence mode when excited at 366 nm and transmission/reflection mode, with the particles dispersed in toluene.

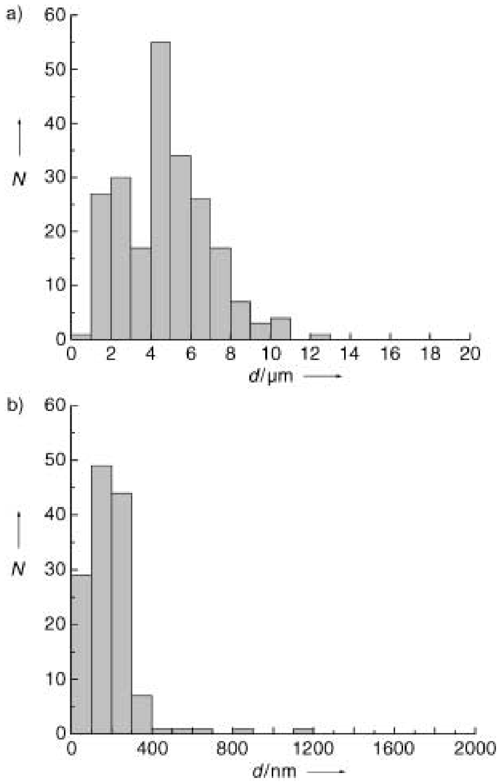

Figure 2. Size-distribution of cross-linked PPE micro- (a) and nanoparticles (b) produced by methods C and D, respectively. The size of the particles was determined from optical-microscopy (a) and scanning-electron-microscopy (b) images. The particles evaluated in (a) were swollen with toluene. N = number of particles, d = diameter.

To further reduce the particle size, the polymerization was conducted by using the conditions outlined above, but an ultrasonic bath was employed for mixing (method D). The yield of the isolated product was limited thus further improvement of the protocol is required, but scanning-electron-microscopy pictures of the redispersed product confirm that cross-linked nanospheres with a diameter of

50–400 nm and a relatively narrow size distribution can be produced by this method (Figure 1c, 2b).

As is evident from Figure 1, the conjugated polymer networks are highly luminescent if swollen with toluene but similar to linear PPEs[14] the luminescence is quenched in the dry solid state. The PL spectra of toluene-swollen milli-, micro-, and nanoparticles produced by methods B–D are shown in Figure 3, together with a reference spectrum of a linear reference polymer[14] dissolved in toluene. Gratifyingly, all materials display very similar emission spectra, which feature well-resolved phonon bands. This result suggests the absence of significant amounts of structural defects and impurities and indicates that neither the network structure, nor the remaining bromine functions significantly disturb the principal optoelectronic properties of the polymers.

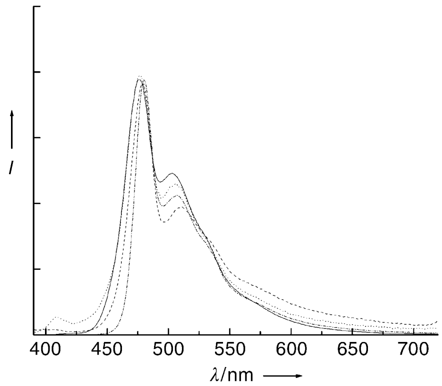

Figure 3. Photoluminescence spectra of PPE milli (method B, dashed line), micro- (method C, dotted line), and nanoparticles (method D, dash-dotted line), suspended in toluene, and an linear PPE reference solution in toluene (solid line).

In conclusion, we have shown that covalently cross-linked spherical conjugated polymer particles can readily be produced by the introduction of adequate cross-linkers and conducting cross-coupling reactions in aqueous macro-, micro-, and miniemulsions. We have demonstrated that the size of the polymer particles can easily be tuned over a wide range (mm to nm) by modification of the reaction conditions. The optoelectronic properties of the materials are similar to those of the linear reference polymer synthesized under conventional conditions, and confirm the absence of electronic defects. Detailed experiments focusing on the charge-transport characteristics of this new class of materials are currently underway.

Experimental Section

Monomers **1** and **2** were prepared as described before.[14] Other chemicals were of the highest available quality and used as received. All reactions were conducted with degassed solvents under Ar atmosphere. IR spectra were measured on KBr pellets on a Bomem MB104 FTIR. Optical microscopy was carried out on an Olympus BX-60 microscope with a spot insight digital camera. PL Spectra were measured under excitation at 366 nm on a SPEX Fluorolog 3 as described previously.[14] Polymers made by methods C and D were redispersed by ultrasonicating the polymers for about 24 h in toluene by using a Fisher Scientific FS-60 ultrasonic bath. SEM images were acquired by using a Hitachi model S-4500.

Method A: **1** (68.0 mg, 0.139 mmol), **2** (71.5 mg, 0.184 mmol), **3** (9.9 mg, 0.031 mmol), $[\mathrm{Pd(PPh_3)_4}]$ (7.5 mg, 0.006 mmol), and CuI (1.0 mg, 0.005 mmol) were combined in a mixture of toluene (2.0 mL) and $i\mathrm{Pr_2NH}$ (1.0 mL). The solution was heated to 70 °C over 24 h. The reaction mixture, which had turned into a fragile gel, was then transferred into stirring toluene (50 mL). MeOH (300 mL) was added at 20 min intervals over the course of 3 h. The product was collected and dried overnight in vacuo at room temperature to yield a brown solid (43.7 mg, 84 %). FTIR: 3438 (m, broad), 3239 (w), 3192 (w), 2955 (s), 2929 (s), 2855 (s), 2738 (w), 2345 (w), 2207 (w, broad), 1870 (w), 1639 (m, broad), 1542 (m), 1508 (s), 1458 (s), 1420 (s), 1388 (s), 1272 (s), 1217 (s), 1150 (w), 1092 (m), 1035 (s), 976 (w), 865 (m), 809 cm^{-1} (m). Elemental analysis calcd: C 80.81 %, H 9.33 %, N 0.00 %, Br 0.00 %; found: C 78.66 %, H 9.93 %, N 0.01 %, Br 1.78 %.

Method B: **1** (73.6 mg, 0.151 mmol), **2** (93.0 mg, 0.240 mmol), **3** (22.3 mg, 0.071 mmol), $[\mathrm{Pd(PPh_3)_4}]$ (7.3 mg, 0.006 mmol), and CuI (1.7 mg, 0.009 mmol) were combined in a mixture of toluene (2.2 mL) and $i\mathrm{Pr_2NH}$ (1 mL). The solution was stirred for 60 s, water (60 mL) was added, and the mixture was heated to 70 °C and vigorously stirred for 24 h. The reaction mixture, in which the organic phase had solidified into many individual, millimeter-sized particles, was cooled to room temperature. The product was isolated by filtration, suspended in toluene (15 mL) and MeOH (100 mL) was added in 20 min intervals over the course of 3 h. The product was collected and dried overnight in vacuo at room temperature to yield brown spherical particles (127.3 mg, 95.6 %). FTIR: 3452 (m, broad), 3056 (w), 2960 (m), 2924 (s), 2854 (s), 2743 (w), 2353 (w), 2208 (m, broad), 1511 (s), 1460 (s), 1420 (s), 1384 (s), 1263 (s), 1215 (s), 1088 (s), 1301 (s), 865 (m), 801 (s), 723 cm^{-1} (m). Elemental analysis calcd: C 80.77 %, H 9.40 %, N 0 %, Br 0 %; found: C 76.17 %, H 8.56 %, N 0.06 %, Br $<$1.76 %.

Method C: **1** (135.8 mg, 0.278 mmol), **2** (144.1 mg, 0.372 mmol), **3** (19.4 mg, 0.061 mmol), $[\mathrm{Pd(PPh_3)_4}]$ (15.0 mg, 0.013 mmol), and CuI (2.3 mg, 0.012 mmol) were combined in a mixture of toluene (4.4 mL) and $(i\text{-}\mathrm{Pr})_2\mathrm{NH}$ (2 mL). The solution was stirred for 60 s, an aqueous solution (60 mL) of SDS (0.8 g) was added, and the mixture was heated to 70 °C and stirred vigorously for 24 h. The reaction mixture, which had turned into an orange suspension, was cooled to room temperature and the solvents were evaporated in vacuo. Toluene (100 mL) was added, and the mixture was ultrasonicated for 1 h. The solid content of the resulting suspension was separated by centrifugation and the supernatant solution was discarded. This procedure was repeated with toluene/MeOH mixtures (3:1, 1:1, and 1:3 *v*/*v*), MeOH, and twice with toluene. The product was collected and dried overnight in vacuo to yield a brown solid (189.8 mg, 89 %). FTIR: 3440 (m, broad), 2963 (s), 2917 (s), 2854 (s), 2332 (w), 2187 (w), 1897 (w), 1638 (m, broad), 1514 (s), 1465 (s), 1420 (s), 1387 (s), 1278 (s), 1218 (s), 1094 (w), 1034 (s), 970 (w), 853 (m), 726 cm^{-1} (w). Elemental analysis calcd: C 80.77 %, H 9.40 %, N 0 %, Br 0 %, S 0 %; found: C 76.91 %, H 8.82 %, N 0.12 %, Br 0 %, S 0.17 %.

Method D: **1** (108.0 mg, 0.221 mmol), **2** (114.9 mg, 0.296 mmol), **3** (15.2 mg, 0.048 mmol), $[\mathrm{Pd(PPh_3)_4}]$ (14.2 mg, 0.012 mmol), CuI (3.5 mg, 0.018 mmol), and SDS (24.3 mg) were combined in a mixture of toluene (3.3 mL), $i\mathrm{Pr_2NH}$ (1.5 mL), and water (9 mL). The mixture was heated to 70 °C in an ultrasonic bath and kept at this temperature for 24 h. The reaction mixture was cooled to room temperature, macroscopic particles were removed by filtration, and the solvents were evaporated in vacuo. Toluene (3 mL) was added to the remaining solid, the mixture was placed into an ultrasonic bath for 24 h, and the suspension was added dropwise into stirring MeOH (100 mL). The solid fraction of the resulting suspension was separated by centrifugation and dried overnight in vacuo to yield a brown solid (7.5 mg, 4.4%).

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[17] We also successfully synthesized the linear PPE based on only **1** and **2** under similar conditions.