


# Synthesis of Conjugated Polymers by Sustainable Suzuki Polycondensation in Water and under Aerobic Conditions

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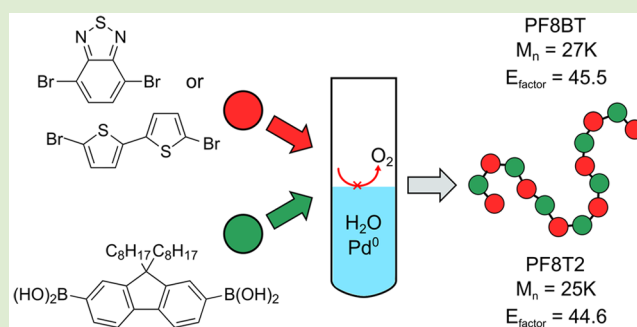
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**ABSTRACT:** Conjugated semiconducting polymers are key materials enabling plastic (opto)electronic devices. Research in the field has a generally strong focus on the constant improvement of backbone structure and the resulting properties. Comparatively fewer studies are devoted to improving the sustainability of the synthetic route that leads to a material under scrutiny. Exemplified by the two established and commercially available luminescent polymers poly(9,9-dioctylfluorene-*alt*-bithiophene) (PF8T2) and poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (PF8BT), this work describes the first examples of efficient Suzuki-Miyaura polycondensations in water, under ambient environment, with minimal amount of organic solvent and with moderate heating. The synthetic approach enables a reduction of the E-factor (mass of organic waste/mass of product) by 1 order of magnitude, without negatively affecting molecular weight, dispersity, chemical structure, or photochemical stability of PF8T2 or PF8BT.



Conjugated polymers play a pivotal role in the development of printed optoelectronics. Examples of the prominence of such polymers can be found in organic photovoltaics (OPV), organic light-emitting devices (OLEDs), organic film effect transistors (OFETs), organic electrochromic devices (OECDs), and light-emitting electrochemical cells (LEECs).<sup>1–6</sup> There is a wide variety of available structural motifs, yet current trends reveal efficient polymers are generally characterized by alternating electron donating or electron accepting building blocks.<sup>7</sup> The synthetic access to such alternating copolymers is dominated by Stille and Suzuki-Miyaura (SM) couplings. The former is notoriously problematic because of the generation of tin-containing toxic waste in stoichiometric amounts. The latter is sizably better in terms of environmental impact yet still requires the activation of one of the two counterparts of the reaction, the use of toxic and harmful organic solvents, and prolonged heating. Improved reaction protocols have been reviewed recently.<sup>8,9</sup> Direct arylation polycondensation (DAP) is emerging as an alternative with improved atom economy. Initial worries regarding regioselectivity and side reactions have been resolved, making this variant a true alternative for coupling mostly thiophene-based monomers.<sup>10–13</sup> However, DAP shares with SM polycondensation (SPC), the common feature of requiring the use of organic solvents, eventually generating organic wastes. The ratio between kg of organic waste produced per kg of products, a number defined as the E-factor, gives a quantitative measure of the comparative sustainability of the process.<sup>14</sup> The removal, or at least a

sizable reduction, of organic solvents has an immediate impact on sustainability.

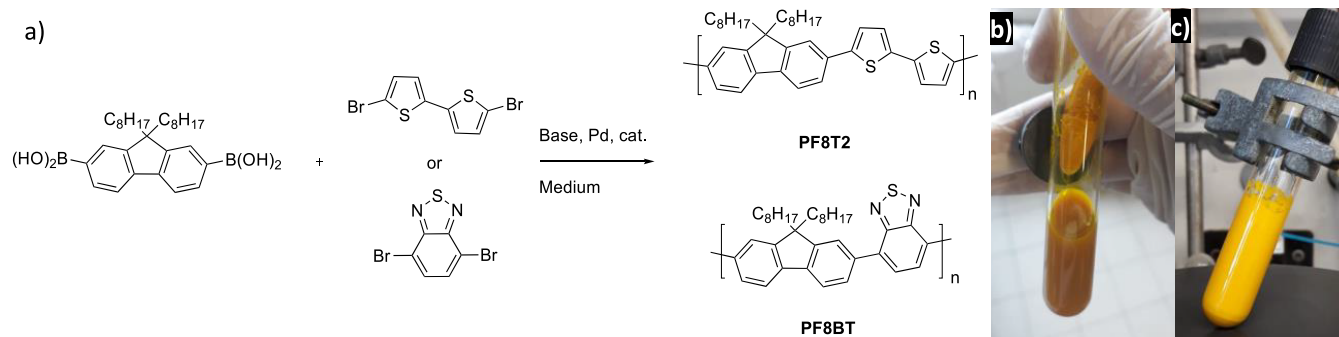
In this context, the last 15 years have witnessed a paradigm shift in the development of sustainable methods for C–C and C–N bond forming reactions, which is the use of water as the main and often only reaction medium.<sup>15</sup> The use of high-performance surfactants enables the formation of various association colloids (micellar solutions, emulsions, dispersions, or microemulsions, depending on the composition of the reactive mixture) when hydrophobic reagents are mixed with water.<sup>16–19</sup> In such microheterogeneous environments, organics are accumulated at very high concentration in low polarity domains, thereby efficiently reacting at high rate, low temperature, and catalyst ppm levels. This phenomenon is known as the “hydrophobic effect”.<sup>20–23</sup> The field of organic semiconductors only recently started to profit from such methods. For instance, reductions in the E-factor by 2 orders of magnitude in the syntheses of relevant molecular semiconductors have been demonstrated using commercially available surfactants.<sup>24–27</sup> However, the extension of such methods to the sustainable synthesis of polymeric semi-

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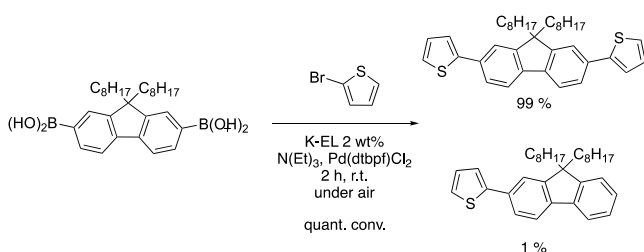


**Figure 1.** (a) Synthesis of 9,9-dioctylfluorene-2,7-diboronic acid with 5,5'-dibromo-2,2'-bithiophene or 4,7-dibromobenzothiazole via SPC to give PF8T2 and PF8BT, respectively; (b) SPC in only K-EL, inhomogeneous; (c) SPC in K-EL/Tol 9:1, freely stirring.

conductors has so far excluded the critical polymerization step. It should be noted that the use of surfactants is well-known in polymer chemistry but so far is limited to polymerization under miniemulsion conditions, where the organic solvent is present in more or less the usual amount. Under such conditions, the focus is the preparation of conjugated organic nanoparticles having specific dimensions and aspect ratio rather than sustainability.<sup>28–31</sup> Indeed, a detailed comparison of the experimental conditions of standard versus miniemulsion polymerization (see Tables S4, S6, S7, and S9 of the SI) does not show an obvious reduction of the characteristic E-factors. Moreover, an inert atmosphere was used throughout.

Here, we applied the “hydrophobic effect”<sup>15</sup> to carry out efficient SPCs with minimal amount of organic solvents under ambient conditions. We selected poly(9,9-dioctylfluorene-*alt*-bithiophene) (PF8T2) and poly(9,9-dioctylfluorene-*alt*-benzothiazole) (PF8BT) as both polymers are commercially available active compounds for the preparation of OLEDs, OPVs, and OFETs (Figure 1a). For both copolymers synthetic protocols in organic solvents are well established, thus enabling straightforward benchmarking of new procedures (see Tables S2 and S3 of the SI). Prior to moving to polymerizations, we investigated the effect of reaction conditions and details of the colloidal state of the mixture on the model reactions between 2,7-dibromofluorene and thienyl-2-boronic acid, as well as on the same counterparts but with reversed functionalities, 9,9-dioctylfluorene-2,7-diboronic acid and 2-bromothiophene. Under ambient conditions with Kolliphor EL (K-EL) as surfactant, 2-bromothiophene and 9,9-dioctylfluorene-2,7-diboronic reacted with quantitative conversion and 1% of monoarylated species as the only discernible byproduct (Scheme 1, see Table S1 of the SI for further details). K-EL is a noionic industrial surfactant obtained by reacting castor oil

### Scheme 1. Model SM Reaction of 9,9-Dioctylfluorene-2,7-diboronic Acid and 2-Bromothiophene in 2 wt % K-EL in Water and under Ambient Conditions



with ethylene oxide. Its composition was recently characterized in detail.<sup>28</sup>

According to the results obtained with the model reactions, we carried out all polycondensations using 9,9-dioctylfluorene-2,7-diboronic acid, 5,5'-dibromo-2,2'-bithiophene, 2 wt % K-EL in deionized water as the surfactant, 4 mol %  $\text{Pd}(\text{dtbpf})\text{Cl}_2$  as the catalyst, and 6 equiv of  $\text{NEt}_3$  as the base. This particular catalyst represents a trade-off between efficiency and affordability. Literature reports more efficient species enabling the sizable reduction of the palladium loading to ppm level.<sup>29</sup> We will explore such custom-made derivatives in the future. Purification was the same for all reactions, including the reference materials (see SI).

Table 1, entry 1, shows the results we obtained working under literature conditions (toluene as solvent, 2 M NaOH as base, 1 mol %  $\text{Pd}(\text{PPh}_3)_4$  as catalyst and heating at 90 °C under an  $\text{N}_2$  atmosphere).<sup>30</sup> Table 1, entry 2, shows the results obtained in water with K-EL that correspond to the best conditions of the test reaction. The reaction is less efficient than the conventional literature method, both in terms of yield and molecular weight. This difference is connected with the microheterogeneous nature of surfactant promoted reactions in water. In the case of the model compound (Scheme 1), the reaction mixture is a dispersion at all stages, which slowly develops the characteristic yellow color of the product. On the contrary, during the synthesis described in Table 1, entry 2, precipitation occurs from the original dispersion, as seen by a sticky lump wrapped around the stirring bar (see Figure 1b). Generally, the success of a micellar catalyzed reaction is connected with the capability of reagents to reach the active catalytic site within the lipophilic pocket. If mass exchange between the water suspension and the association colloids is prevented, exactly the case of the phase separation observed in the polymerization reaction, a controlled chemical reaction is excluded. Literature reports indicate similar effects for poorly soluble products.<sup>31</sup> The common solution is the use of small amounts of organic solvents, on the order of 10 vol % with respect to water, which effectively turns the micellar solution in an emulsion.<sup>31,32</sup> Such a strategy has a negligible impact on sustainability as the amount of toluene is very small: roughly 20 mg every 100 mg of monomer mixture. We have previously explored such a technique in the synthesis of latent pigments via S-M in K-EL/toluene mixtures.<sup>33,34</sup> The dynamic light scattering (DLS) characterization shows that whereas K-EL alone in water gives micelles having a 12 nm average diameter, the addition of monomers and toluene leads to the formation of an emulsion with average droplet dimension in the 1  $\mu\text{m}$  regime (Figure S1 of the SI). Table 2, entry 3, shows this type

**Table 1.** Suzuki Polycondensation According to Scheme 1 to Give PF8T2 (Entries 1–5) and PF8BT (Entries 6–9)

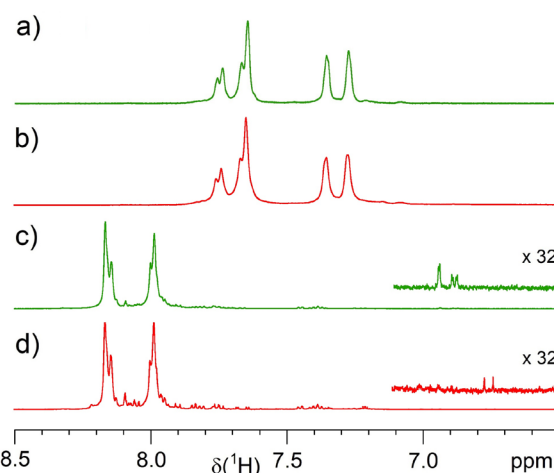
entry/polymer	medium <sup>a</sup>	base	catalyst (mol %)	T (°C)	atm	yield (%)	M <sub>n</sub> (kg/mol)	M <sub>w</sub> (kg/mol)	Đ
1 - PF8T2	toluene	NaOH	Pd(PPh <sub>3</sub> ) <sub>4</sub> (1)	90	N <sub>2</sub>	94	24.2	39.8	1.64
2 - PF8T2	K-EL	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (4)	25	air	70	15.9	26.3	1.65
3 - PF8T2	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (4)	25	air	72	20.7	34.8	1.68
4 - PF8T2	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (4)	60	air	72	20.5	37.0	1.81
5 - PF8T2	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (4)	80	air	87	25.2	49.4	1.96
6 - PF8BT	H <sub>2</sub> O/Tol .2:1	K <sub>2</sub> CO <sub>3</sub>	Pd <sub>2</sub> (dba) <sub>3</sub> /P( <i>o</i> -Tol) <sub>3</sub> (2)	95	N <sub>2</sub>	90	11.3	20.1	1.65
7 - PF8BT	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (2)	25	air	77	6.8	11.0	1.54
8 - PF8BT	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (2)	80	air	93	19.7	38.3	1.94
9 - PF8BT	K-EL/Tol .9:1	NEt <sub>3</sub>	Pd(dtbpf)Cl <sub>2</sub> (4)	80	air	90	26.9	50.9	1.89

<sup>a</sup>K-EL stands for 2 wt % solution of Kolliphor EL in deionized water.

of experiment. The addition of 10 vol % toluene helps avoid macroscopic phase separation (see Figure 1c for visualization). Molecular weight increases moderately from 15.9 to 20.7 kg/mol. Further improvements required the increase of the temperature from r.t. to 60 (entry 4) and 80 °C (entry 5), eventually achieving results comparable with literature data for polymerizations carried out under inert atmosphere and with organic solvents.<sup>30,35,36</sup> We performed one such polymerization (entry 1) in order to have a standard for comparative characterizations (vide infra) and to gather information for a reliable estimate of the E-factor. The value we obtained (entry 1, E-factor 229) is significantly larger than that calculated for entry 5 polymerization (E-factor 45, see Tables S4 and S5 of the SI for details).

The difference by a factor of 6 is remarkable, especially considering that the same result can be obtained under ambient conditions, which greatly facilitates the entire experimental procedure. We tested the generality of our water-based protocol for the structurally related PF8BT that is synthesized from the same boronic acid and 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole via SPC as well. As for the previous case, we first performed the reaction under literature conditions in order to get a direct comparison as well as to gather all the information required for the estimate of the E-factor. Table 1, entry 6, shows the results obtained using a biphasic toluene/water 2:1 mixture as the reaction medium, K<sub>2</sub>CO<sub>3</sub> as the base, and Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub> as the catalyst. Entries 7–9 show the results obtained from K-EL/toluene 9:1 emulsion with using Pd(dtbpf)Cl<sub>2</sub> as catalysts. Working at 80 °C and in the presence of a 10 vol % amount of toluene (Table 1, entry 9), we obtained a M<sub>n</sub> of ~27 kg/mol. This value is higher than that obtained in our control experiment and in line with the results described in the literature for similar SPCs in organic solvents.<sup>37–42</sup> On comparing the E-factor of our protocol (46) and the literature procedure (209), we find a difference by a factor of 4.5.

To further judge on structural integrity of the obtained products, <sup>1</sup>H NMR spectroscopy was performed at 120 °C in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. Figure 2a,b shows the aromatic region of the spectra of PF8T2 from entries 4 and 1, respectively (for the entire spectra, see the Supporting Information). From this comparison, a difference between the two samples is not discernible and evidence for defects<sup>30</sup> is not seen either, which is further corroboration for the usefulness and advantages of the herein presented protocol. Similarly, the aromatic regions of the <sup>1</sup>H NMR spectra of the PF8BT control (Figure 2d, Table 1, entry 6) and the sample by polymerization in water (Figure 2c, Table 1, entry 8) are comparable. One difference between PF8BT made by micellar polycondensation and in homoge-

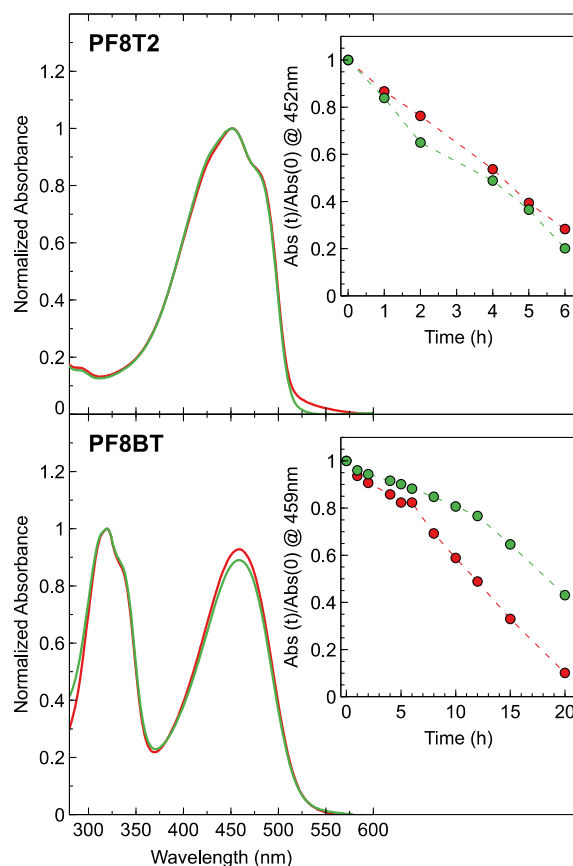


**Figure 2.** (a, b) Comparison between the <sup>1</sup>H NMR spectra (regions) of PF8T2 samples. Trace (a) corresponds to Table 1, entry 4, sample polymerized in water; (trace b) is the Table 1, entry 1, control experiment. (c, d) PF8BT samples. Trace (c) corresponds to Table 1, entry 8, sample polymerized in water; trace (d) is Table 1, entry 6, control experiment. The insets in c and d show the intensified region in which OH-termination of the fluorene end groups appears around 6.95 ppm.

neous medium is, however, the presence of OH-termination at the F8 unit for the former at ~6.95 ppm (compare insets of Figures 2c,d). This type of end group is a result of oxidative deborylation and stems from the presence of oxygen in the reaction medium.<sup>43</sup> We previously demonstrated that K-EL micelles have an oxygen free core, yet such a characteristic does not extend to the interphase with the hydrophilic shell.<sup>44</sup>

In a standard micellar reaction on molecular materials, most of the reaction events are taking place in the core but some of them will also happen close to the interphase region. While working with molecular materials, a simple purification would easily get rid of the few percent of oxidized byproducts. In the case of a polymerization, such parasite process will just act as a termination, in our case competing with protodeborylation. Such an effect does not alter optical properties (vide infra) and does not sizably influence the polymerizations, as the molecular weight are comparable with those obtained with standard techniques. Further small signals between 7.2 and 8.1 ppm stem from additional end groups both present in entries 6 and 8, which differ in intensity due to their different molar mass. We also compared the optical properties of the polymers prepared in water with those of the reference materials. As shown in Figure 3, the UV–vis absorption in both cases is almost identical to the benchmarks. Molecular weight,





**Figure 3.** Normalized UV–vis spectra of thin films of PF8T2 and PF8BT samples prepared by standard methods (red lines, entries 1 and 6 in Table 1) and micellar method (green lines, entries 5 and 8 in Table 1). Inset: photooxidation under white-light irradiation.

termination, and defectivity are known to impact both on optical properties of conjugated polymers and durability.

The latter can be considered a “litmus test” to assess the quality of the obtained materials. We thus submitted both PF8T2 (Table 1, entries 1 and 5) and PF8BT (Table 1, entries 8 and 6) to extended photostability tests. PF8T2 samples showed essentially indistinguishable kinetics of degradation upon light irradiation (Figure 2, top inset). In the case of PF8BT, entry 8 exhibited improved stability. As degradation commonly starts from the end groups, with further properties being otherwise almost identical compared to the control sample, the improved photostability of the micellar samples is likely due to its higher molecular weight. As mentioned, the minor OH-termination does not affect stability negatively.

In conclusion, we have shown that micellar SPC in water is a viable tool for the preparation of conjugated polymers, as exemplified by PF8T2 and PF8BT. Once reaction conditions are optimized in terms of temperature and compositions of the medium, it is possible to prepare both PF8T2 and PF8BT with properties at least as good as controls made under homogeneous, common catalytic SPC.

We chose K-EL as the preferred surfactant for our approach, as it is economic and commercially available, enables a reduced E-factor of the polymerization by 1 order of magnitude, and finally allows to carry out the reaction under ambient conditions. We assume this method is generally applicable to both copolymers of interest for printed electronics and photovoltaics, as well as to other cross-coupling variants such

as direct C–H activation polycondensation. These aspects, along with a characterization of the residual amount of palladium in the purified polymers, are currently the subject of ongoing investigations.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00495>.

Detailed information about the synthesis of model compounds and polymers. Extensive optimization of model reactions for the preparation of PF8T2 and PF8BT. Comparative evaluation of the E-factors of all described and literature reactions. Comparison between polymerization statistics obtained with micellar and several organic solvent-based literature methods. Complete photochemical characterization of the samples, including UV–vis, profilometry, and FT-IR spectra as a function of the exposition time. DLS analysis of the reaction mixture with and without toluene (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

K-EL Kolliphor EL; Pd(dtbpf)Cl<sub>2</sub> [1,1'-bis(ditert-butylphosphino)ferrocene]dichloropalladium(II); Pd(PPh<sub>3</sub>)<sub>4</sub> tetrakis(triphenylphosphine)palladium(0); Pd<sub>2</sub>(dba)<sub>3</sub> tris-(dibenzylideneacetone)dipalladium(0); P(*o*-Tol)<sub>3</sub> tri(*o*-tolyl)-phosphine

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