

# A New Solution to an Old Problem: Synthesis of Unsubstituted Poly(*para*-phenylene)

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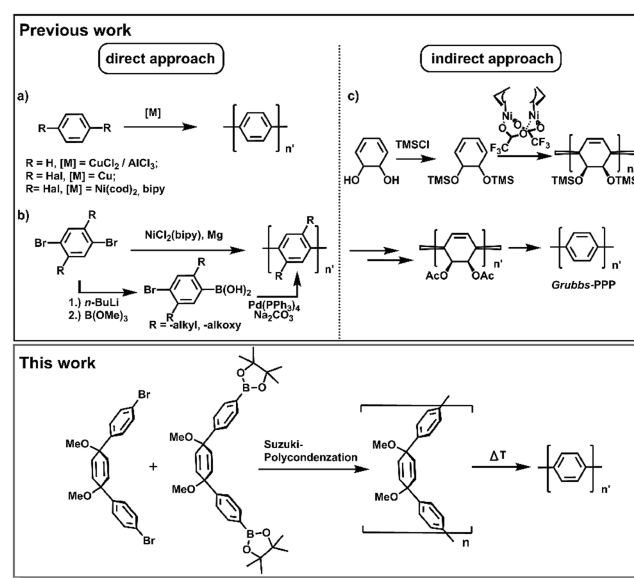
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**S** Supporting Information

**ABSTRACT:** Unsubstituted and structurally well-defined poly(*para*-phenylene) (PPP) has been long-desired as an organic semiconductor prototype of conjugated polymers. To date, several attempts to synthesize unsubstituted, pristine, high-molecular-weight PPP have failed. Here we solved this synthetic problem by a versatile precursor route. Suzuki polymerization of kinked disubstituted 1,4-dimethoxycyclohexadienylene monomers yielded a well-soluble, nonaromatic precursor polymer. Its solubility allowed processing by spin-coating into nanometer-thick films. Subsequent additive-free thermal treatment induced aromatization and led to exclusively *para*-connected, highly fluorescent PPP with a length of about 75 phenylene units.

As the prototype of a conjugated polymer, unsubstituted and structurally well-defined poly(*para*-phenylene) (PPP) has been the quest of various synthetic approaches. In neutral form, PPP is an insulator, whereas upon doping its conductivity increases to  $500 \Omega^{-1} \text{ cm}^{-1}$ .<sup>1</sup> Its compressive strength (207 MPa), low density ( $1.210 \text{ g cm}^{-3}$ ), and high stability toward temperature, oxygen, and moisture render PPP a promising candidate for applications in organic electronics.<sup>2</sup> In the past, several routes toward PPP have been developed. Since short *para*-phenylene oligomers ( $\leq 6$  phenylenes) are barely soluble in common organic solvents, all direct aryl–aryl couplings via 1,4-dihalobenzenes lead to regioselectively formed but very short oligomers (Scheme 1a).<sup>3</sup> The oxidative coupling of benzene results in a significant amount of ortho-connected and hence ill-defined phenylene units.<sup>4</sup> Longer PPP ( $n \approx 30$ ) can be obtained by the introduction of solubilizing side chains (alkyl/alkoxy groups) at the ortho positions (Scheme 1b),<sup>5</sup> but unfortunately, this results in low charge carrier mobility and an undesired blueshift of the emission bands due to deplanarization of the polymer backbone.<sup>6</sup> Recently, several approaches for the surface-assisted synthesis of PPP have been published.<sup>7</sup> Drawbacks of this approach are the requirement of the high Miller index metal surfaces, the obtained low quantity of PPP, lack of follow-up processability, and high experimental effort. A promising strategy toward unsubstituted PPP is the so-called precursor route, by which Grubbs was able to successfully address the problem of regioselectivity (Scheme 1c).<sup>8</sup> Although

Scheme 1. Different Synthetic Approaches toward PPP<sup>3–7</sup>



precursor polymers for subsequent syn-elimination reactions were obtained, structurally perfect and unsubstituted PPP without impurities (e.g., acid residues) has not been achieved to date.<sup>9</sup>

We sought to overcome the above-mentioned obstacles to the synthesis of regioregular high-molecular-weight PPP by pursuing a novel precursor approach. Herein we report the first facile synthesis of unsubstituted, structurally well-defined PPP. By the use of kinked monomers containing disubstituted cyclohexadienylene moieties, good solubility is introduced into the resulting precursor polymer. Furthermore, this cyclohexadienylene is convertible to a phenylene unit by aromatization reactions. Hence, processing of thin films from solution, subsequent additive-free thermal aromatization to form PPP layers, and their optical characterization are enabled.

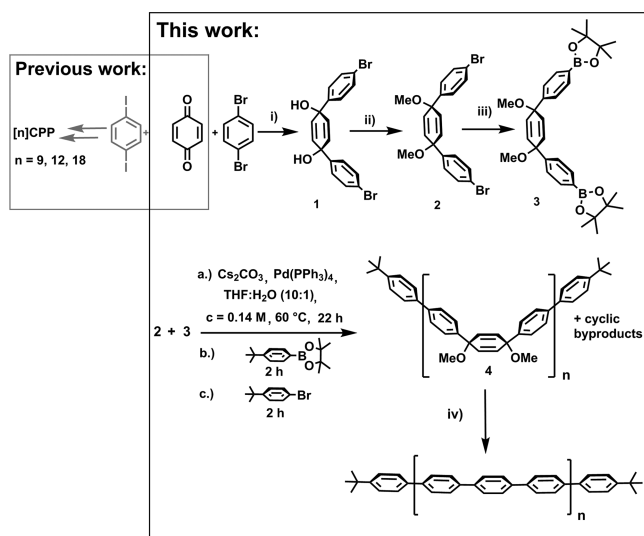
For our PPP synthesis, we utilized chemistry previously developed for [*n*]-cyclo-*para*-phenylenes ([*n*]CPPs).<sup>10</sup> The

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reported *syn*-1,4-bis(4-halophenyl)-1,4-dimethoxycyclohexadienes (e.g., Scheme 1, bottom) could be used not only for the synthesis of macrocycles but also for linear poly(*para*-phenylene). Monolithiation of 1,4-dibromobenzene with *n*-butyllithium and subsequent twofold coupling to *p*-benzoquinone led to 1,4-bis(4-bromophenyl)-1,4-dihydroxycyclohexadiene (**1**). Dihydroxy intermediate **1** was methylated quantitatively with methyl iodide to give 1,4-bis(4-bromophenyl)-1,4-dimethoxycyclohexadiene (**2**). After lithiation followed by transmetalation of **2**, bis(boronic ester) **3** was obtained in 76% yield. The *syn* isomers **2** and **3** were polymerized by Suzuki–Miyaura cross-coupling (AA/BB type) and subsequently terminated with *para*-substituted phenylene bromide and boronic ester to attain the precursor polymer **4** (Scheme 2). To estimate the chain length via  $^1\text{H}$  NMR spectroscopy, we

**Scheme 2. Synthesis of Monomers and (Precursor) Polymer<sup>a</sup>**



<sup>a</sup>Conditions: (i) *n*-BuLi, THF,  $-78\text{ }^\circ\text{C}$ ; (ii) NaH, MeI, THF,  $0\text{ }^\circ\text{C}$ ; (iii) *n*-BuLi, isopropoxyboronic acid pinacol ester, THF,  $-78\text{ }^\circ\text{C}$ ; (iv)  $<300\text{ }^\circ\text{C}$ .

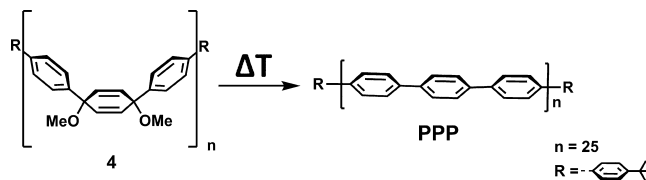
chose *p*-*tert*-butylbenzene for end-capping. In polycondensations two competitive reactions, i.e., polymerization and macrocyclization, occur.<sup>11</sup> In our synthetic approach, two strategies to suppress macrocycle formation could be considered: Use of the corresponding anti isomer should inhibit CPP precursor formation, since the conformational preorientation would result in chain growth in opposite directions and thus lower the tendency for macrocyclization. Since the more desirable anti isomer is synthetically not available, the polymerization conditions for *syn*-1,4-bis(4-bromophenyl)-1,4-dimethoxycyclohexadiene were adjusted.<sup>12</sup> Thus, the polymerization was performed under kinetically controlled conditions at a monomer concentration of 0.14 M, which is 10 times higher than for  $[n]$ CPP synthesis, to reduce the tendency to form macrocycles.<sup>10a,11,13</sup> Isolation of the target polymer **4** was successfully carried out by fractionated precipitation, as the cyclic and oligomeric byproducts remained dissolved because of their higher solubility (see the Supporting Information (SI)). This method generally allows the synthesis and purification of the precursor polymer on a gram scale, whereas separation of the cyclic and linear macromolecules

is not feasible via conventional chromatographic methods because of their similar polarities and hydrodynamic radii.

The molecular weight distributions of the obtained fractions were estimated via analytical gel permeation chromatography (GPC) versus polystyrene standards (Table S1). In the purified PPP precursor (yield  $\approx 10\text{ wt }%$ ,  $M_w = 11\,130\text{ g/mol}$ ), a single broad peak with a polydispersity index (PDI) of 2.10 was observed after GPC analysis from THF, which is expected for a step-growth polymerization. As insoluble polymeric residues were removed before quantification, we obtained a polymer with a chain length of at least  $n_{M_n} = 18$  and  $n_{M_w} = 38$ , which means 54 and 115 phenylene units, respectively, after aromatization (see the SI). Chain length could be determined even more accurately from the relative intensities of  $^1\text{H}$  NMR signals of the aromatic and olefinic parts with respect to the *tert*-butyl end-group resonances, resulting in an estimated degree of polymerization of  $n_{\text{NMR}} = 25$  (75 phenylenes). Hence, NMR analysis is in full agreement with the values obtained from GPC analysis (see the SI).

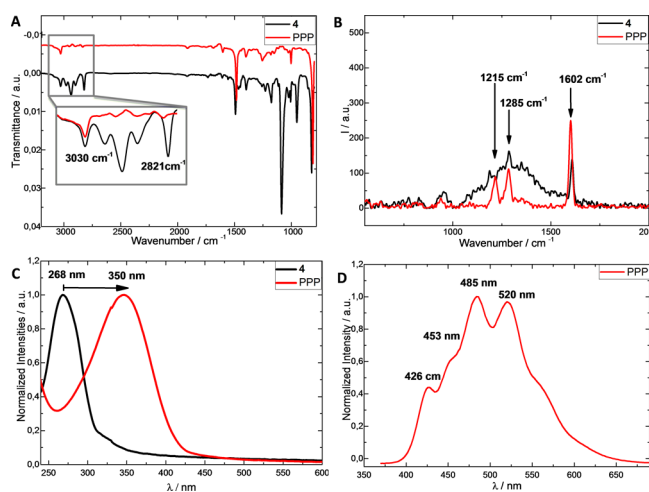
The conversion of precursor polymer **4** into PPP was realized by a facile, solely thermal aromatization protocol for thin films to yield highly fluorescent PPP films. Because of insolubility and lack of follow-up processability of the target PPP, the right choice of the conditions for aromatization of **4** was crucial. A solution-based aromatization—similar to CPP synthesis with, e.g., sodium naphthalenide—was impractical since the polymer would precipitate before completion of the reaction, leaving undefined products. As polymer **4** is well-soluble in chloroform, thin films could be readily prepared. A spin-coated sample with a thickness of approximately 20 nm was heated to  $300\text{ }^\circ\text{C}$  (2 h) to give fluorescent PPP consisting of approximately 75 phenylene units (Scheme 3). The aromatization temperature

**Scheme 3. Aromatization by Thermal Annealing of Thin Films**



was determined by thermogravimetric analysis (TGA) of the bulk polymer. The TGA trace shows a loss in mass of the precursor polymer at about  $225\text{--}300\text{ }^\circ\text{C}$ . This mass loss is attributed to demethoxylation to yield the corresponding phenylene units (see the SI).

The quantitative aromatization of thin films (ca. 20 nm) was investigated by IR spectroscopy, which revealed typical bands expected for exclusive PPP formation. The most instructive band for PPP is the “out-of-plane” C–H stretching mode of the *para*-disubstituted phenylene moiety at  $810\text{ cm}^{-1}$ . Furthermore, C(sp<sup>2</sup>)–H stretching modes generally appear above  $3000\text{ cm}^{-1}$  (here at  $3030\text{ cm}^{-1}$ ), which is expected for a polymer exclusively constructed entirely from sp<sup>2</sup>-hybridized carbons. Especially the band at  $2821\text{ cm}^{-1}$ , which is characteristic of the methoxy groups of the precursor polymer, disappears completely after annealing as a clear proof of quantitative conversion into PPP (Figure 1A). For further validation, Raman spectroscopy was conducted. The spectra reveal three bands expected for PPP ( $1215$ ,  $1285$ , and  $1602\text{ cm}^{-1}$ ; Figure



**Figure 1.** (A) Compared IR spectra of PPP (red) and precursor polymer **4** (black). (B) Raman spectra (785 nm) of PPP (red) and **4** (black). (C) UV/vis spectra of **4** (black) and PPP (red). (D) Fluorescence spectrum of the PPP ( $\lambda_{\text{ex}} = 350$  nm).

1B), consistent with the bands described for *para*-phenylene oligomers.<sup>14</sup>

The aromatization leads to a  $\pi$  extension that is apparent from UV/vis spectra of the thin films (the optical properties are summarized in Table 1). A bathochromic shift of the

**Table 1. Summary of the Optical Properties of PPP**

$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)	Stokes shift (cm <sup>-1</sup> )	$\Delta E_{\text{gap}}$ (eV)	$\Theta$ (%)
347	426, 453, 485, 520	8200	2.94	18

absorption maximum by almost 80 nm (from 268 nm for the precursor polymer to 347 nm for PPP) is observed (Figure 1C). The PPP films show bright emission in the range of 400–600 nm (Figure 1D). Quantum yields ( $\Theta$ ) were determined with an Ulbricht sphere and amount to 18% in thin films. The emission spectrum exhibits four well-structured bands at 426, 453, 485, and 520 nm, with one shoulder at 550 nm. This is in good agreement with those of oriented *p*-sexiphenyl films and oriented *para*-phenylene oligomer films.<sup>15</sup> In addition, excitation of the aromatized PPP film at the absorption maximum of **4** does not show any emission band attributed to the precursor polymer (see the SI), which supports full conversion of **4** to PPP.

In summary, by the use of an elaborate precursor route, access to the long-desired unsubstituted poly(*para*-phenylene) (PPP) in its pristine form has been established. Polymerization of kinked monomers containing cyclohexadienylene units under Suzuki conditions yielded the regioregular and well-soluble high-molecular-weight precursor polymer **4**. Additive-free aromatization of **4** in thin films solely by thermal treatment afforded PPP of unrivaled length (ca. 75 phenylenes) and purity compared with previously reported precursor routes or direct aryl–aryl coupling protocols (vide supra). Structural perfection of the resulting PPP was confirmed via vibrational spectroscopy, as evidenced by the absence of residual methoxy bands (IR) and the presence of three bands expected for PPP (Raman). The annealing procedure without the need of any additives allows direct utilization of thin-film PPP in organic electronics, as it can be readily incorporated into the fabrication process of, e.g., printed multilayer devices. In the future, our research will

focus not only on OLEDs based on PPP as an emissive material but also on the utilization of our precursor route for the controlled surface-assisted synthesis of graphene sheets by lateral expansion of aligned PPP on high Miller index surfaces.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10254.

General information, synthetic procedures, purification protocol for **4**, GPC analysis, NMR spectra, film forming and annealing protocol, TGA data for **4**, investigations of aromatization by absorption and fluorescence spectroscopy, and crystal structures of the monomers (PDF)  
 Crystallographic data for **1** (CIF)  
 Crystallographic data for **2** (CIF)  
 Crystallographic data for **3** (CIF)

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### Notes

The authors declare no competing financial interest.

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