

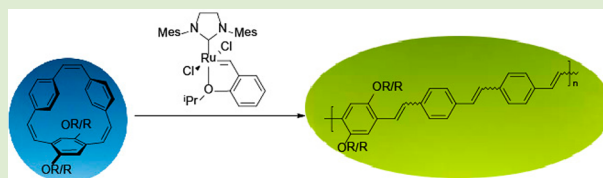
[2.2.2]Paracyclophane-Trienes—Attractive Monomers for ROMP

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Supporting Information

ABSTRACT: Three derivatives of 4,7-substituted [2.2.2]-paracyclophane-trienes were synthesized and used in ring-opening metathesis polymerization (ROMP), resulting in well-soluble poly(*para*-phenylenevinylene)s (PPV). The paracyclophane-trienes were prepared using an iterative buildup of a phenylene-ethynylene backbone, followed by a *cis* selective Grignard reduction and an intramolecular McMurry reaction. The monomers were applied in ROMP to result in well-soluble PPV derivatives with an unusual substituent pattern. The PPVs were spin-coated into amorphous, highly fluorescent films. To the best of our knowledge, we are the first to synthesize 4,7-substituted [2.2.2]paracyclophane-trienes and use them as ROMP monomers.



Due to their spectacular optical and optoelectronic properties, conjugated polymers such as polyfluorene,¹ polythiophene,² poly(phenyleneethynylene) (PPE),³ or poly(*para*-phenylenevinylene) (PPV)⁴ have been studied intensely.⁵ Their potential as semiconductors in applications such as organic field-effect transistors (OFET),⁶ organic photovoltaics (OPV),⁷ or organic light-emitting diodes (OLEDs)⁸ is significant.

PPV might be the most examined semiconducting polymer. Unsubstituted PPV has successfully been exploited for OLEDs⁹ and OPVs.¹⁰ Due to the parents' poor solubility, it is processed out of a precursor polymer by extrusion of leaving groups, as studied by Wessling et al., which gives the parent PPV.¹¹ If solubilizing groups are attached to the PPV backbone, processable PPVs with controlled morphology are accessible.¹² Dozens of different side chains were attached to the PPV backbone, highlighting relationships between polymer structure, photoluminescence yield, and efficiency of electroluminescence.^{13,14}

Substituted and soluble PPVs are synthesized by Gilch-type, Pd-catalyzed, and other methods.^{15–18} Acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) of suitable precursors is an attractive alternative for defect-free PPVs.¹⁹ After Bazan et al. studied the ROMP of paracyclophanes into PPV precursor polymers,²⁰ Turner et al. elegantly developed a direct ROMP-approach of substituted [2.2]paracyclophane-dienes giving PPV-homo-²¹ and -block-copolymers.^{22,23} However, the paracyclophane-diene monomers are difficult to synthesize, yet ROMP is a suitable and powerful method for the *direct* synthesis of soluble PPV derivatives with low polydispersities.

Inspired by Müllen et al.²⁴ and Oda et al.²⁵ we contended that larger cyclophanes might have enough strain energy to give ROMP-able monomers. We found that unsubstituted [2.2.2]-paracyclophane-triene follows ROMP into insoluble PPV. The (*E,Z,E,Z*)-isomer²⁵ of [2.2.2.2]paracyclophane-tetraene is also

ring-opened into PPV, whereas the (*Z,Z,Z,Z*)-isomer does not have enough strain energy to be active (Figure 1).²⁵

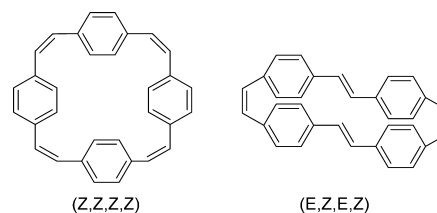


Figure 1. Structures of the [2.2.2.2]paracyclophane-tetraenes.

Herein we report the synthesis of dodecyl-, dodecyloxy-, and 2-ethylhexyloxy substituted [2.2.2]paracyclophane-trienes **4a–c** as monomers of well-soluble PPVs with an unusual substituent pattern. We developed a new synthetic route for these [2.2.2]paracyclophane-trienes and applied them in ROMP to give the PPVs **5a–c**.

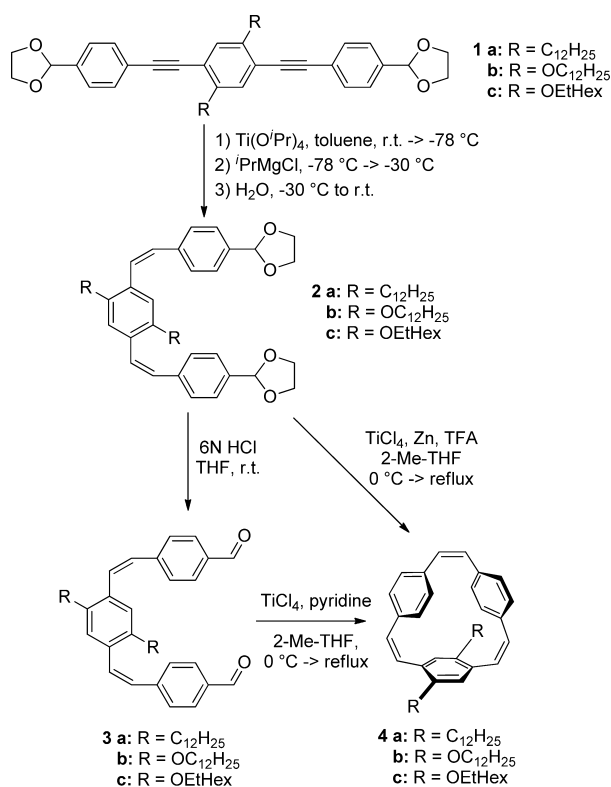
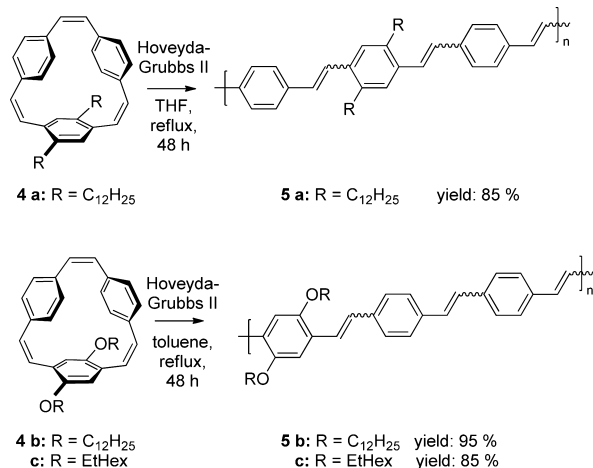
Scheme 1 shows the key synthetic steps. In the original synthesis of the parent **4**, Tanner et al. used a Wittig reaction building up the *cis* double bonds. Trying the same with *para*-substituted benzene derivatives led to a mixture of *cis* and *trans* isomers, hardly separable. Consequently, we developed an alternative route. Sonogashira-Hagihara coupling gives **1a–c**, which are easily and *cis* selectively transformed into **2a–c** through a Grignard reduction.²⁶

For cyclization we used the McMurry reaction but encountered several problems. Deprotection of acetals **2a–c** with hydrochloric acid in THF yields crude dialdehydes **3a–c**, which can be purified by column chromatography. Unfortunately, when dissolved, **3a–c** isomerize rapidly. The yield of the desired all-*cis* isomers drop. Nevertheless, **3a–c** can be coupled

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Scheme 1. Synthesis of 4,7-Substituted [2.2.2]Paracyclophane-Trienes 4a–c

Scheme 2. Polymerization of Monomers 4a–c to PPV Derivatives 5a–c


in an intramolecular McMurry reaction, yielding the 4,7-substituted [2.2.2]paracyclophane-trienes **4a–c**.

To avoid the problem of isomerization of **3a–c**, we employed the configurationally stable acetals **2a–c** in the intramolecular McMurry reaction.²⁷ Acceptable yields are obtained (100 mg ~40%) on small scales but yields drop upon scale-up, and the competing intermolecular polymerization becomes prevalent. Reductive ring closure, yielding a single instead of a double bond, is another side reaction when using **2a–c**, complicating purification.

The solution to the problem of isomerization and low yields during scale-up is the simple omission of the purification of the dialdehydes **3a–c**. Dioxolanes **2a–c** are deprotected by diluted

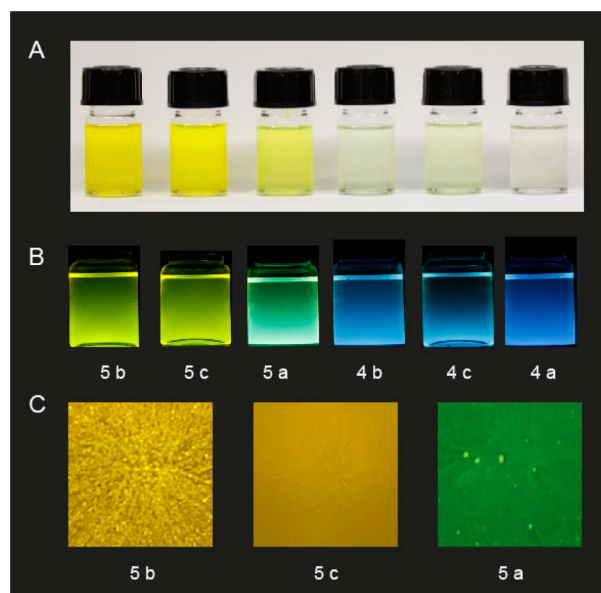


Figure 2. Photographs of (A) absorption and (B) emission under ultraviolet illumination (365 nm) of polymer and monomer solutions in CHCl₃. (C) Photographs of spin-coated films out of C₆H₅Cl under ultraviolet illumination (365 nm).

hydrochloric acid, overnight in the dark. Phase separation, filtration through a plug of silica, and evaporation of the solvent under light exclusion give **3a–c** with a nearly complete all-cis configuration according to ¹H NMR. The dialdehydes **3a–c** were directly applied in the pseudo high dilution McMurry cyclization using a syringe pump, protected with aluminum foil. The [2.2.2]paracyclophane-trienes **4a–c** are obtained in good yields (55–64%) after scaling up. This is higher than the yields published for similar systems.^{24,28,29} **4a–c** were isolated as pale yellow-colored oils which show weak fluorescence in their pure and dissolved states.³⁰

Aromatic proton signals in ¹H NMR spectra are high-field shifted, overlapping with vinylic signals, reflecting the electronic interaction within the system. Surprisingly cyclophanes **4a–c** are oils, in contrast to their unsubstituted parent molecule³¹ or their ortho substituted derivatives.²⁹

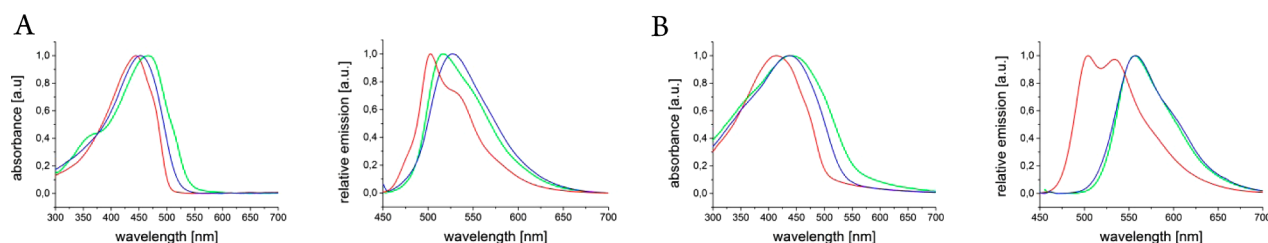
In Scheme 2, ROMP of **4a–c** into PPVs **5a–c** is shown; Table 1 summarizes the properties of the resulting PPVs. Polymerization of **4a** at room temperature yields PPV **5a** with a polydispersity of 2.8. Increasing the temperature lowers the polydispersity of **5a** to 1.9, assuming that higher temperatures improves the initiation of ROMP of **4a**. The alkoxy substituted derivatives **4b** and **4c** do not show any reaction at room temperature or in refluxing THF. A change to the higher boiling solvent toluene (110 °C reaction temperature) produces PPVs **5b** and **5c** with polydispersities of 1.4 and 1.7.

The higher reaction temperature is necessary due to the oxygen in the side chains of **4b,c**, which works as anchor group for the catalyst, inducing an energy barrier for ROMP. ¹H NMR spectroscopy of polymers **5a–c** (see Supporting Information) shows a trans/cis ratio about 59–70%, respectively, indicating that the double bonds formed during ROMP are mostly trans-configured and those that are not opened by ROMP tend to isomerize easily (calculated trans/cis ratio: 33%).³² Thermogravimetric analysis of the polymers indicates no weight loss up to 300 °C. As metathesis is quite sensitive to steric effects, we assume that the double bond

Table 1. Summary of Polymeric, Optical, and Electronic Properties of **5a–c**

polymer	M_n^a (kDa)	M_w^a (kDa)	PDI ^a	$\lambda^{Abs}(CHCl_3)$ (nm)	$\lambda^{Em}(CHCl_3)$ (nm)	Φ^b	$\lambda^{Abs}(\text{film})$ (nm)	$\lambda^{Em}(\text{film})$ (nm)	$E_g(\text{opt})^c$ (eV)	HOMO ^d (eV)	LUMO ^e (eV)
5a	29.5	56.5	1.9	444	502, 528	0.60	414	504, 534	2.42	−5.45	−3.03
5b	26.9	37.8	1.4	466	517	0.50	446	556	2.18	−5.37	−3.19
5c	11.4	19.5	1.7	453	529	0.49	438	558	2.28	−5.27	−2.99

^aDetermined by gel-permeation chromatography using $CHCl_3$ as solvent (polystyrene standards). $PDI = M_w/M_n$. ^bQuantum yield determined using the comparative method to fluorescein. ^cOptical band gap in thin films, graphically determined by extrapolating the linear part of the absorption. ^dCV of polymer films on Pt electrode in MeCN containing 0.1 M *n*-Bu₄NPF₆. $HOMO = -(4.8 + E_{pa})$. E_{pa} was extrapolated in ferrocene corrected plot. ^eLUMO = HOMO + $E_g(\text{opt})$.

**Figure 3.** Absorption and emission spectra of polymers **5a** (red), **5b** (green), and **5c** (blue) in $CHCl_3$ (A) and spin-coated out of C_6H_5Cl (B).

attached to the two unsubstituted benzene ring is the most active one in ROMP.

Figure 2 gives an impression of the color and emission of monomers **4a–c** and polymers **5a–c**. Alkoxy monomers and polymers show red-shifted optical features. Photographs of spin-coated preparations reveal that **5c** forms more homogeneous films, perhaps due to the bulkier side chains. All films of **5a–c** are amorphous according polarizing optical microscopy.

Optical spectroscopy of PPVs **5a–c** was performed in solution ($CHCl_3$) and in the solid state (Figure 3). The absorption features of alkoxy-PPVs **5b** and **5c** are red-shifted in comparison to that of polymer **5a**. The small difference in absorbance between **5b** and **5c** might occur because of the higher molecular weight of **5b**, reflecting a longer chain length. Comparison of polymers **5b** and **5c** with the optical features of other alkoxy-substituted PPVs prepared by ROMP show similar absorption wavelengths.²³ Polymer **5a** shows a typical PPV emission spectrum with a maximum and a distinct, red-shifted shoulder. Absorbance and emission are in accordance with that of literature known PPVs.³³ Quantum yields, however, are significantly higher than of those prepared in similar studies.^{23,32}

Thin films of PPVs **5a–c** were fabricated by spin-coating of a solution of the polymers (10 mg/mL in chlorobenzene) and drying on a hot plate for 15 min at 150 °C. In contrast to other studies, the absorption of all three polymers is blue-shifted in the films, when compared to their solution spectra (**5a**: 30 nm, **5b**: 20 nm, **5c**: 15 nm). In emission, a redshift is observed for polymers **5b** and **5c**. **5a** does not experience a redshift, but the ratio between the emission maximum and shoulder changes.

The investigation of polymer thin films by polarizing optical microscopy did not show any thermal behavior. The films stayed amorphous up to 180 °C. No crystallization was observed upon cooling.

Oxidation potentials and HOMO energies of PPVs **5a–c** were determined through cyclic voltammetry (CV) by drop-casting a thin film onto a platinum working electrode in a 0.1 M solution of *n*-Bu₄NPF₆ in acetonitrile (Table 1). LUMO energies were determined by the correlation between band gap and HOMO energies: $E_g = LUMO - HOMO$. The alkoxy substituted polymers **5b** and **5c** have a smaller band gap than

the alkyl substituted polymer **5a** because of the electron donating effect of oxygen. The higher HOMO/LUMO energies of **5c** compared to that of **5b** might be caused by differences in molecular weight and subtle influences of the side chains on the structure of **5a,b** in the amorphous solid state.

In summary, easily prepared trimeric cyclophanes **4a–c** are ROMP-active and give rise to amorphous PPV derivatives **5a–c**, employing a second generation Hoveyda-Grubbs catalyst at enhanced reaction temperatures. PPV-derivatives **5a–c** are formed with respectable molecular weights and have an unusual substitution pattern but are surprisingly well soluble. They form amorphous films by spin-coating. The modular synthesis of monomers offers the possibility to introduce different building blocks and will be investigated in future to expand the field of [2.2.2]paracyclophane-trienes, creating a library of novel PPV derivatives with unusual substitution patterns and properties.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental section with preparation of monomers and polymerization; ¹H and ¹³C NMR, HR-MS, elemental analysis, gel-permeation chromatography, cyclic voltammetry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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