Synthesis and Polymerization of an *Ortho-Para*-Substituted Tetraalkoxy [2.2]Paracylophane-1,9-diene

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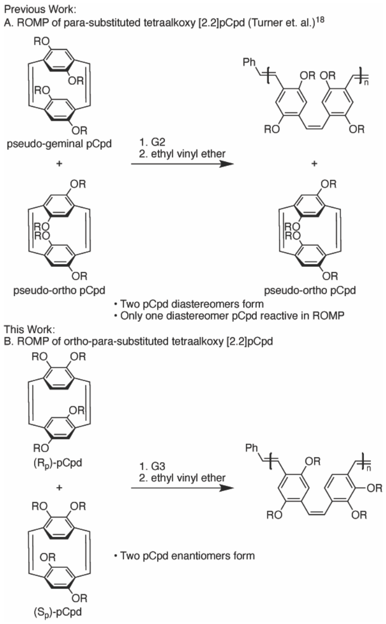
ABSTRACT: This contribution describes the synthesis of an unsymmetrical substituted tetraalkoxy[2.2]paracylophane-1,9-diene comprised of an *ortho*-substituted and a *para*-substituted dioctyloxybenzene. (S_p)-4,5,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene ((S_p)-pCpd) and (R_p)-4,5,13,16-tetraoctyloxy-[2.2]paracyclophane-1,9-diene ((R_p)-pCpd) are formed as planar chiral enantiomers. Unlike other tetraalkoxy-substituted pCpds that form as diastereomers, both the (S_p)-pCpd and the (R_p)-pCpd can be polymerized via ring-opening metathesis polymerization (ROMP) using Grubbs' third generation initiator (G3) as it is achiral. Living ROMP afford copolymers featuring alternating *cis,trans*-poly(*p*-phenylene vinylene)s (PPV)s. The polymers' unique, blue-shifted optical properties are due to the alkoxy-substitution in the polymer's backbone and the resulting materials could be photo-isomerized to the all-*trans* polymer. This strategy affords tetraalkoxy-pCpd monomers in high yields for the polymerization of soluble PPVs with low or narrow dispersities.

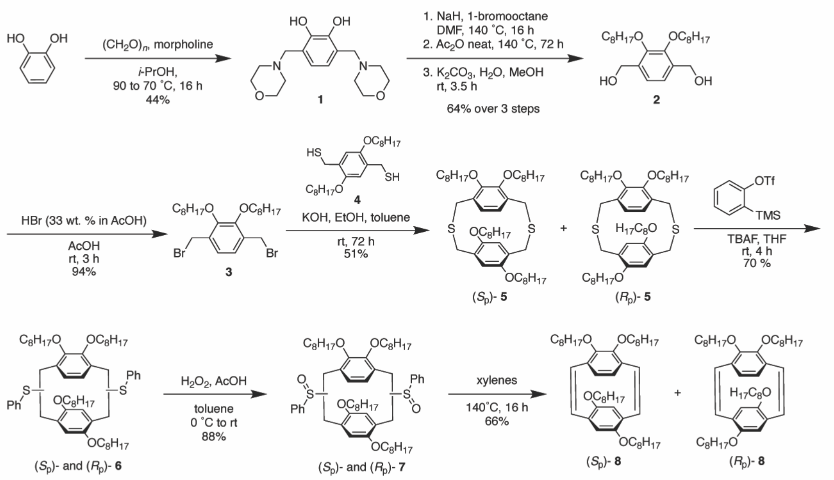
Poly(*p*-phenylene vinylene) (PPV), a π-conjugated conductive polymer, has potential applications in polymer electronics and as optoelectronic materials.[1] PPVs have been used as the emissive layer in an organic light emitting diode (OLED) in 1990[2] with more recent applications of PPVs and its oligomers as chemical and biological sensors,[3] for fluorescent imaging,[4] and as building blocks in supramolecular polymers.[5-7] When unsubstituted, PPV, a rigid-rod polymer, is insoluble.[8] Alkoxy side-chains can be appended to the benzene repeat units in the backbone to improve solubility but they inherently influence the optical properties of the final polymer. *Para*-substituted poly(2,5-dialkoxy-1,4-phenylene vinylene)s have primarily been investigated due to the ease of preparing their corresponding monomers and a bathochromic shift in emission (both in solution and the solid state), compared to the unsubstituted parent PPV, is a result of a reduction of the polymer's band gap.[9] When alkoxy side-chains are substituted in an *ortho*-fashion, poly(2,3-dialkoxy-1,4-phenylene vinylene)s display a hypsochromic-shift in the emission maximum.[10] This clearly demonstrates that the placement of electron-donating side-chains has an significant impact on the optical properties of PPVs.

Commonly practiced synthetic routes towards PPV, such as the Gilch method, Wessling method, or cross-coupling strategies primarily result in polymers with poor control over molecular weights and dispersities and often have significant incorporation of backbone defects which alters their performance in devices.[1, 9] Instead, the ring-opening metathesis polymerization (ROMP) of [2.2]paracyclophane-1,9-diene (pCpd) to yield PPVs is a chain-growth polymerization with a high degree of control. The reason is pCpd's high strain energy of greater than 40 kcal mol^{-1},[11] which is favorable for a controlled polymerization and the ROMP of pCpd yields defect-free PPVs with narrow dispersities and control over the polymer's end groups and configuration of alkene stereochemistry.[12-14] Additionally, this strategy is advantageous as it easily lends itself to the formation of block copolymers.[15-17] Given the high degree of polymer structural control imparted by ROMP, the limited scope of pCpds reported in literature restrict the variety of conjugated polymers accessible by this method.



Scheme 1. A) ROMP of the all *para*-substituted tetraalkoxy-[2.2]paracyclophane-1,9-diene diastereomers with Grubbs' second generation initiator.[18] B) ROMP of unsymmetrically substituted *ortho-para*-tetraalkoxy-[2.2]paracyclophane-1,9-diene isomers. R= *n*-C_8H_{17}

Poly(2,5-dialkoxy-1,4-phenylene vinylene)s have been synthesized by Turner and coworkers starting from an all-*para*-substituted tetraalkoxy-pCpd monomer. This highly strained pCpd was accessed in an overall yield of 7% over four steps.[19] Due to the substitution pattern of the all-*para*-tetraalkoxy pCpd, two diastereomers form: the pseudo-*ortho* isomer and the pseudo-



Scheme 2. Synthesis of planar chiral enantiomers (S_p)-4,5,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene and (R_p)-4,5,13,16-tetraoctyloxy-[2.2]paracyclophane-1,9-diene. **6** and **7** are drawn to represent both the S_p and R_p isomers present in a 50:50 mixture.

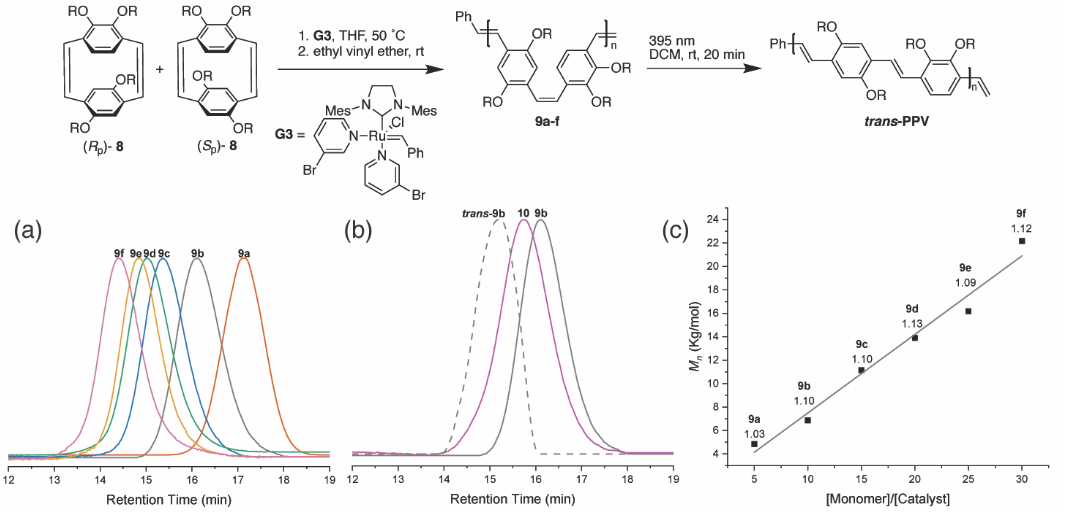


Figure 1. GPC (a) GPC chromatogram of block extension studies. (B) GPC chromatogram showing the change in retention time of *cis/trans*-**9b** with the block copolymer **10** and the photoisomerized *trans*-**9b**. (C) Plot of M_n as a function of [**8**]/[**G3**]. R= *n*-C_8H_{17}, GPC in THF using the UV-vis detector

geminal isomer in a 5 to 4 diastereomer ratio. Steric constraints provide that only the pseudo-*geminal* isomer, the minor of the two can be polymerized via ROMP as one face of the olefin is not blocked by the alkoxy-side-chains enabling the coordination of the ruthenium (Scheme 1).[18] Herein, we describe a synthetic method that affords an unsymmetrically substituted *ortho-para*-tetraalkoxy-pCpd. Due to the mixed substitution of this pCpd, all afforded monomer is easily polymerized with Grubbs 3rd generation initiator (**G3**) ~~under the same conditions~~. The living polymerization of this *ortho-para*-tetraalkoxy-pCpd monomer was investigated along with its blue-shifted optical properties. We additionally demonstrate the photoisomerization of the *cis/trans*-PPV copolymers to the all-*trans* PPV copolymer, which is unique to this polymerization method and can find applications in photo-switchable materials.

To synthesize *ortho*-substituted pCpds, bis(bromomethyl) *ortho*-octyloxybenzene **3** is a key building block. Using common bromomethylation reagents (HBr in acetic acid and paraformaldehyde) results in *ortho*-alkoxysubstituted benzenes being *meta*-bromomethylated rather than the desired *para*-bromomethylation.[20-22] Instead, to access **3,** the Mannich reaction with catechol affords bis-Mannich base **1**. Octyl-chains are then appended and the Mannich base is exchanged over two steps to afford diol **2** which can be precipitated out in large quantities using cold hexanes. This is then converted to the desired bromomethylated compound **3** using 33 wt. % hydrogen bromide solution in acetic acid in high yields (Scheme 2).

To afford the target tetraalkoxy pCpd, the *ortho*-substituted dibromide was combined with *para*-substituted dithiol **4** at low concentrations to afford the [3.3]dithiaparacyclophane **5** as two planar chiral enantiomers, (S_p)-**5** and (R_p)-**5** in a 51% yield. A benzyne-induced Stevens rearrangement, followed by oxidation to the [2.2]paracyclophane bis(sulfoxide), allowed for the successful pyrolysis-induced elimination to afford pCpd **8** in an overall yield of 21% over 4 steps as (S_p)-4,5,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene ((S_p)-**8**) and (R_p)-4,5,13,16-tetraoctyloxy-[2.2]paracyclophane-1,9-diene ((R_p)-**8**) which are not separable by common synthetic techniques (Scheme 2). As no chiral catalysts or chiral auxiliaries were used in this synthesis, a statistical one-to-one mixture of the enantiomers of compounds **5** and **8** are expected. Samples of **5** and **8** were analyzed via chiral HPLC, confirming the racemic mixtures (Figure S1 and S2). Both, (S_p)-**8** and (R_p)-**8**, have one face of an alkene that is not blocked by an octyloxy-side-chain

Table 1. GPC data and optical characterization of *ortho-para*-substituted PPVs.

PPV	[**8**]/[**G3**]	M_n, calc[a]	M_n, GPC[b]	Đ	% yield	Abs. λ_{max} (nm)[c]	Em. λ_{max} (nm)[c]
9a	5	3690	4800	1.03	89	413	522
9b	10	7275	6900	1.10	86	416	524
9c	15	10861	11000	1.10	94	420	524
9d	20	14447	14000	1.13	91	419	525
9e	25	18032	16000	1.09	87	420	526
9f	30	21618	22000	1.12	86	422	526
trans-9b	-	7275	14000	1.05	quant.	470	523

[a] M_n calculated values were calculated based on the targeted degree of polymerization (noted in [**8**]/[**G3**]). [b] M_n GPC values were determined against polystyrene standards. [c] Measurements were done in dilute solutions of chloroform.

allowing for easy coordination of the achiral Ruthenium catalyst to form the desired π-complex. This is in contrast to the all-*para*-substituted tetraalkoxy-pCpds where only the *pseudo*-geminal isomer is able to coordinate to the ruthenium complex (Scheme 1).[18] *In situ* NMR experiments using **8** and **G3** in THF-d_8 at 50 °C ([**8**]/[**G3**] = 10) confirmed that both (S_p)-**8** and (R_p)-**8** undergo ROMP to form the PPV copolymer with greater than 95% conversions after 67 hours (Figure S3).

We then investigated the living nature of the ROMP of **8** (Figure 1). We observed a linear relationship of the monomer to initiator ratio ([**8**]/[**G3**]) with molecular weight (M_n) collected from gel permeation chromatography (GPC) in THF (Figure 1c). All polymers have low or narrow dispersities ($Đ$ = 1.03-1.13) and achieve full monomer consumption. Furthermore, a block copolymer (**10**) was formed by introducing another pCpd monomer in a subsequent ROMP step (Scheme S1) and a consistent shift in molecular weight is observed (Figure 1b). These findings strongly support that **8** is polymerized in a living manner.[23]

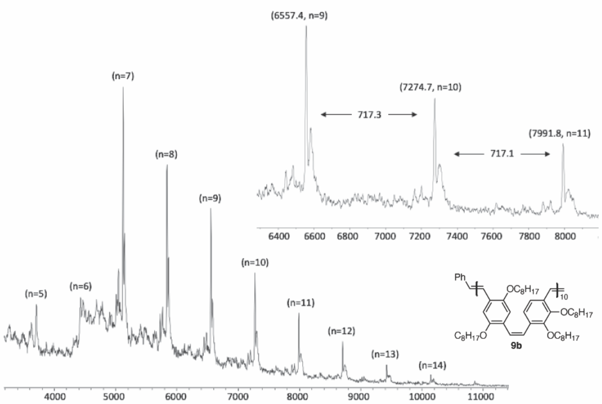
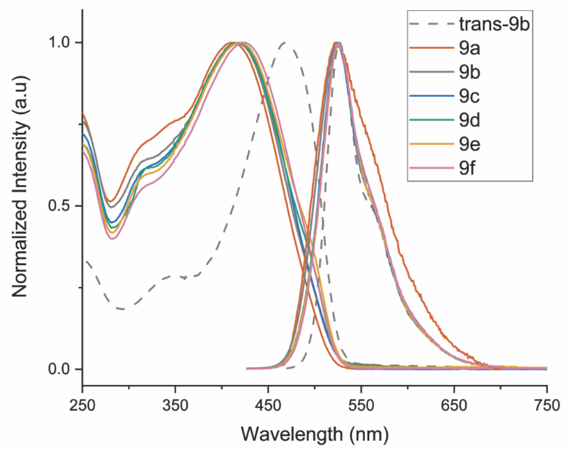


Figure 2. MALDI-TOF mass spectrum of polymer 9b.

The end groups of **9b** were examined using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. A series of major peaks separated by intervals of 717 amu corresponds to the molecular weight of the monomer (Figure 2). The observed mass is consistent with a PPV capped with a phenyl group from the initiation with **G3** and a vinyl group from the termination with ethyl vinyl ether, as expected in a living polymerization (n = 10, the mass found m/z 7274.7 expected mass 7275.5).

The ROMP of pCpds with Grubbs' initiators, regardless of sidechains or arene units, result in PPVs with alternating *cis/trans*-vinylene stereochemistry.[24-27] The isomerization of **9b** to the all-*trans* PPV structure (***trans*-9b**) was achieved by irradiating the polymer solution in a photoNMR tube. A dilute solution of **9b** in degassed dichloromethane-d_2 was placed in the outer chamber of the tube while an optical cable with a wavelength of 395 nm was fed into the inner chamber to penetrate the solution. ^{1}H NMR spectra of the solution in the photoNMR tube recorded before and after exposing the solution to UV light shows the complete disappearance of the -OCH$_2$ protons in the *cis* stereoisomer at δ 3.54 ppm ~~and a broadening of the~~ while the *trans* stereoisomer peak from δ 4.09-4.05 ppm remain (Figure S7). The GPC analysis of ***trans*-9b** also shows lower retention times than its *cis/trans*-counterpart which is consistent with a coil-to-rod transition resulting in a larger hydrodynamic volume for the all-*trans* isomer (Figure 1b). This ability to fully isomerize PPVs without incorporating defects into the polymer is significant as the all-*trans* material performs better in devices.[9]

Figure 3. Normalized absorbance and emission spectra of PPV copolymers **9a-f** and the photoisomerized ***trans*-9b**.



The optical properties of the polymers were measured in dilute solutions of chloroform (Figure 3 and Table 1). All *cis,trans*-PPV copolymers (**9a-f**) feature absorbance maxima around 419 nm while ***trans*-9b** has a 54 nm red-shifted absorbance, a result of the increased conjugation length. Excitation of the polymers at their absorbance maximum, regardless of their alkene stereochemistry, result in a green emission (λ_{max} = 524 nm). This is similar to reported 2,3-dibutoxy PPVs prepared by the Gilch route displaying an emission maximum at 530 nm but their polymers have a dispersity of 5.5 or greater.[9-10, 28-29] The optical properties of our *ortho-para*-octyloxy-substituted PPV copolymers are blue-shifted 30 nm from its all-*para*-octyloxy-substituted PPV counterpart synthesized with the same strategy.[19]

In summary, we report the synthesis of [2.2]paracyclophane-1,9-diene with an *ortho*-alkoxybenzene substituent. When an unsymmetrically substituted pCpd is assembled with both a 2,3-

octyloxybenzene and a 2,5-octyloxybenzene, two planar chiral enantiomers form as a racemic mixture in an overall yield of 21%. Both enantiomers of the unsymmetrically substituted *ortho-para*-tetraalkoxy-pCpd can be polymerized via ROMP using Grubbs' third generation initiator to afford *cis,trans*-PPV copolymers. The living nature of the polymerization was confirmed, and it was demonstrated that the PPV copolymers can be rapidly photoisomerized using UV light to the all-*trans* isomer. Investigation of the optical properties show a green fluorescing polymer that is blue-shifted 30 nm in emission compared to its 2,5-dioctyloxy PPV counterpart afforded by the same methods. This change in optical properties can be attributed to the incorporation of *ortho*-alkoxy substitution into the polymer's backbone. This work is an important expansion of tetraalkoxy-substituted-pCpds as all afforded monomer is polymerizable and endows each benzene unit in the PPV with two alkoxy-side chains, necessary for the solubility of the conjugate polymer. We anticipate this access to *ortho*-alkoxy pCpds will enable further explorations of newly substituted pCpds and their structure-property relationships in PPVs and PPV containing materials.

Supporting Information

Full experimental details, Chiral HPLC data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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