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Supramolecular bottlebrush copolymers from crown-ether functionalized poly(*p*-phenylenevinylene)s†

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The discovery of living, chain-growth polymerizations of poly(*p*-phenylenevinylene)s (PPVs) allows for low dispersed, controlled, and architecturally complex PPV-based polymers. This contribution presents the synthesis of PPVs functionalized with crown-ethers on each repeat unit that assemble with chain-end functionalized monotelechelic poly(styrene)s (PS) containing a terminal amine salt to form pseudorotaxane-based bottlebrush copolymers. The PPVs are synthesized by living ring-opening metathesis polymerization (ROMP) and the PS through atom-transfer radical polymerization (ATRP). The bottlebrush copolymer formation was confirmed by nuclear magnetic resonance spectroscopy, gel-permeation chromatography, isothermal titration calorimetry, dynamic light-scattering, wide-angle X-ray scattering, and optical spectroscopy. This work depicts the first example of a backbone modified PPV synthesized through ROMP and introduces a versatile strategy towards supramolecular bottlebrush copolymers containing conducting polymers. Our methodology lends itself to supramolecular materials for applications in chemical sensing, optoelectronics, and fluorescent imaging.

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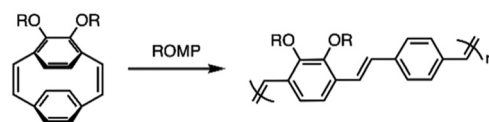
Introduction

Organic conducting polymers, such as poly(*p*-phenylenevinylene) (PPV), are π -conjugated polymers with desirable optical and electrical properties.¹ PPVs have been used in devices such as organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and as fluorescent probes in biomedical applications.² Substituting PPVs with solubilizing side-chains, such as alkoxy groups, makes this rigid-rod polymer solution processable.³

The discovery of living chain-growth polymerization of cyclophanedienes to yield PPVs using ruthenium catalysts has unlocked the development of well-defined PPV-based materials, with tuneable properties (Scheme 1).^{3,4} [2.2] *para*-cyclophanediene (*p*Cpd) is polymerized by ring-opening metathesis polymerization (ROMP) to yield PPVs in a living, chain-growth manner with control over molecular weights, dispersities, and end-group identities.^{4,5} The living character of ROMP also allows for the formation of block copolymers.⁶ Recently, the Weck group reported dealkylating *para*-substituted *p*Cpds with complex side-chains that can be polymerized.^{7,8}

Macromolecular architecture impacts polymer properties, such as packing, glassy states, melt temperatures, crystallinity, viscosity, and optical activity.^{9–12} Bottlebrush copolymers are composed of linear polymers emanating from a main-chain, whose identity and density impacts polymer properties.¹³ Linear PPVs have been widely reported but more complex PPV architectures are rare and PPV-based bottlebrush copolymers have not been reported to date.^{7,14,15}

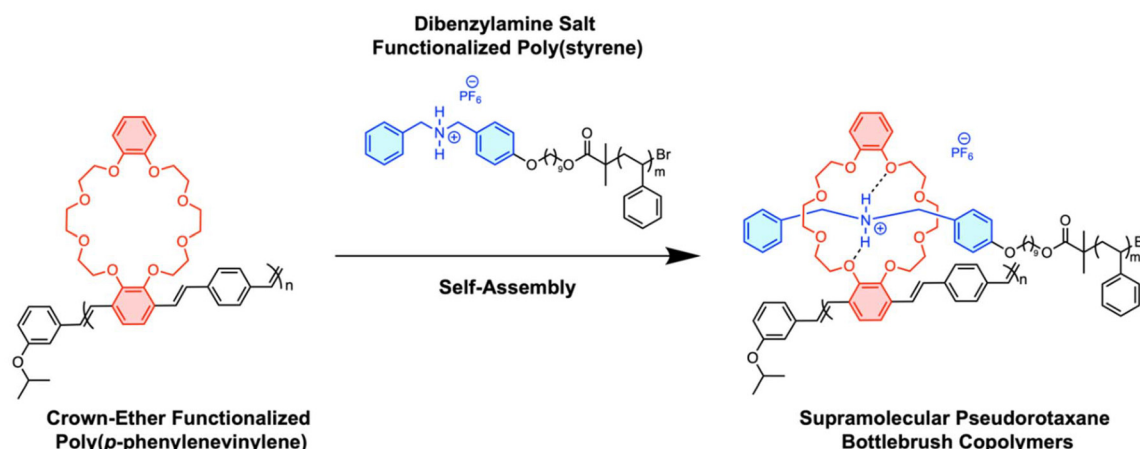
Over the past decade, to gain control over macromolecular architecture, the Weck group used molecular recognition units (MRUs) featuring noncovalent interactions such as hydrogen bonding, metal coordination, or π - π stacking to directionally self-assemble polymers into complex 3D structures.^{16–21} Macroyclic crown-ethers are prominent MRUs that form host-guest complexes with a range of both inorganic and organic cations.^{17,22,23} Combining hydrogen bonding, coulombic interactions, electrostatic forces, and size complementarity, crown-ethers can recognize specific alkali metals and ammonium salts, resulting in the formation of pseudorotaxanes.^{24–26} We



Scheme 1 Ring-opening metathesis polymerization (ROMP) of *ortho*-substituted-alkoxy-[2.2] *para*-cyclophanediene. R = alkyl side-chain.

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Scheme 2 Synthesis of supramolecular bottlebrush copolymers based on host–guest interactions between crown-ether functionalized poly(*p*-phenylenevinylene) and dibenzyl amine end-functionalized poly(styrene).

rationalize that installing crown-ethers and ammonium salts on two separate polymers, one along each repeat unit of polymer A and the other at the terminus of polymer B, supramolecular bottlebrush copolymers can be constructed (Scheme 2).^{18,27–29}

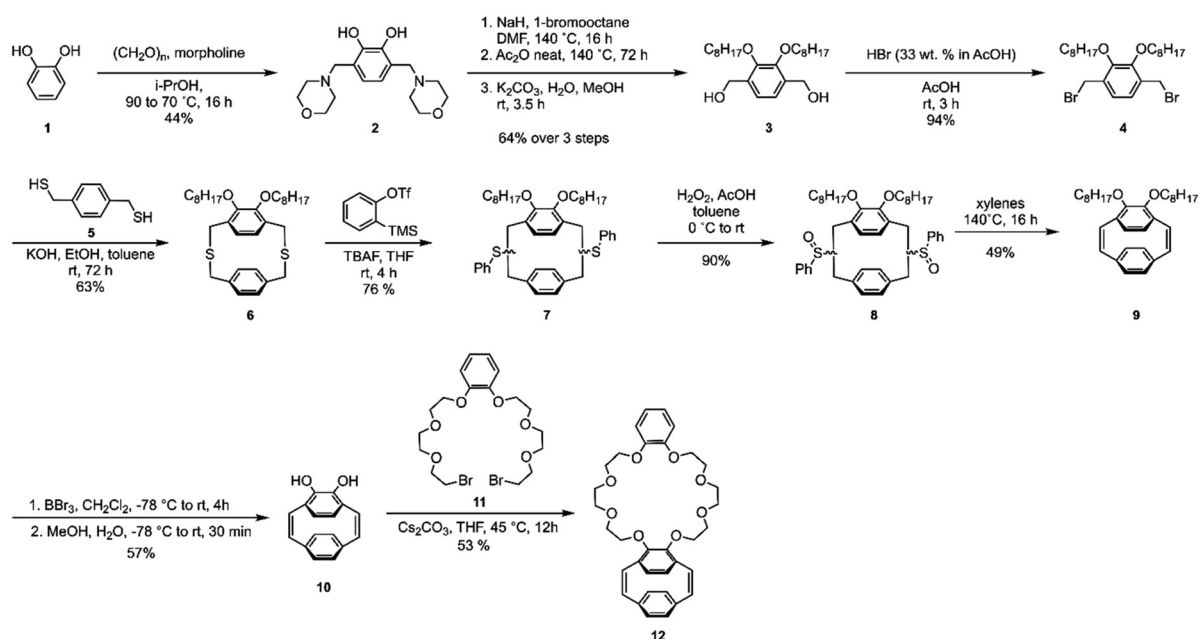
In this contribution, we report the realization of a PPV-based supramolecular bottlebrush copolymer (Scheme 2). Our design is based on *ortho*-substituted *p*Cpds appended with dibenzo-24-crown-8 (DB24C8) and polymerized *via* ROMP to afford crown-ether containing PPVs (CE-PPVs). Using atom-transfer radical polymerization (ATRP), poly(styrene) (PS) was functionalized with a complementary cationic dibenzyl ammonium (DBA⁺) at one chain-end (PS-DBA⁺).³⁰ Pseudorotaxane formation yielded supramolecular bottle-

brushes which were characterized by nuclear magnetic resonance (NMR) spectroscopy, gel-permeation chromatography (GPC), isothermal titration calorimetry (ITC), dynamic light-scattering (DLS), wide-angle X-ray scattering (WAXS), and optical spectroscopy. Our work provides a platform to develop supramolecular functionalized materials for applications in areas such as sensing, optoelectronics, and fluorescent imaging.

Results and discussion

Synthesis

The *ortho*-substituted *p*Cpd, **9**, was synthesized in close analogy to our previous report, starting with catechol.⁷



Scheme 3 Synthetic route towards CE-*p*Cpd, **12**.

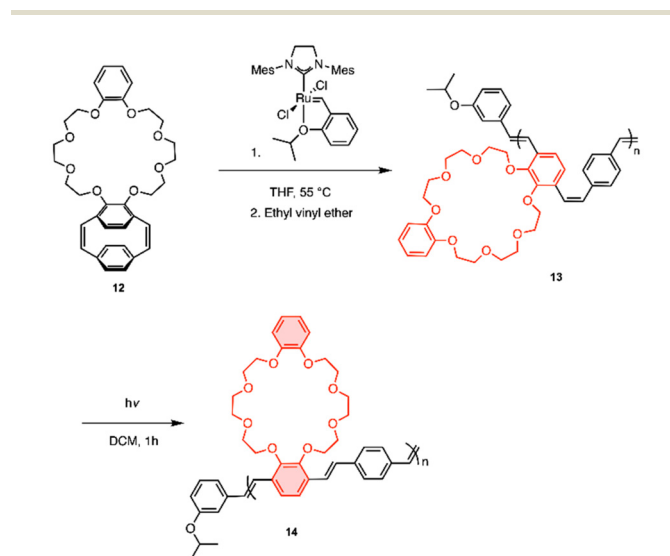
Morpholine groups were installed using a Mannich reaction. For solubility, alkoxy groups were appended and the Mannich base was exchanged over two steps to afford diol **3** which was converted to the dibromomethylated product, **4**. Under dilute conditions, **4** was reacted with **5** to form the [3.3] dithia-*para*-cyclophane **6**. Compound **6** underwent a benzyne-induced Stevens rearrangement to give compound **7**, which was oxidized to form compound **8**. The sulfoxides were thermally eliminated to contract the ring resulting in diene **9**. Compound **9** was treated with boron tribromide to generate the catechol-like *p*Cpd **10**. It should be noted that when *para*-substituted *p*Cpds undergo dealkylation, the dihydroxide oxidizes to form diquinones. The same was not observed with the *ortho*-substituted *p*Cpd.³¹ Compound **10** was reacted with dibromide **11** under basic conditions to give the desired crown-ether *p*Cpd (CE-*p*Cpd) monomer **12** (Scheme 3).

We investigated the living nature of the ROMP of **12** (Scheme 4) using Hoveyda-Grubbs' second generation initiator (HGII) (Fig. 1). All resulting polymers showed low dispersities

($D < 1.33$) with full monomer consumption (Fig. 1a). We observed a linear relationship for each of the monomer to initiator feed ratios ($[M]/[I]$) plotted with the molecular weights (M_n) (Fig. 1b) (**13a–d**). ROMP gives PPVs with a *cis-trans* conformation that can be photo-isomerized under UV-light to give the all-*trans*-CE-PPV, **14**. The absolute molecular weights were determined by ^1H NMR spectroscopy by integrating the isopropoxy protons on the initiating end-group from HGII and comparing them to the methylene protons. The livingness of the polymerization was further elucidated by preparing a diblock copolymer, which supported the presence of an active chain-end (**15**) (ESI, Scheme S2†). Again, complete monomer consumption was observed by *in situ* ^1H NMR spectroscopy and end-group identity by ^1H NMR spectroscopy and MALDI-ToF-MS (ESI, Fig. S3†). These results show that the polymerization proceeded without chain-termination or chain-transfer and the resultant polymers had low dispersities with control over polymer properties, *i.e.*, **13** was polymerized in a living, chain-grown manner.^{31,32}

The optical properties of the PPV polymers were then investigated. Consistent with previous literature, as the molecular weight of the CE-PPVs increased, the absorbance maxima decreased while emission remained similar (Table 1).³³ Compared to *para*-substituted PPVs, the CE-PPV's blue-shifted absorbance and emission wavelength maxima are consistent with *ortho*-substitution of PPVs as reported in the literature.^{7,33,34} Previously, the Weck group published the synthesis of *ortho-para*-substituted tetra-alkoxy PPVs.⁷ These PPVs absorb at 416 nm and emit at 524 nm, whereas the CE-PPVs absorb at 353 nm and emit at 483 nm. The substituent identity and location differ between these two PPVs. The crown-ether substituent has a significant impact on the hypsochromic shift of both optical parameters. When the *cis-trans*-CE-PPV (**13b**) photo-isomerized to the all-*trans*-**14**, the absorbance red-shifted and emission remained the same, consistent with increasing conjugation length due to lower steric crowding around the *trans* vinylene bonds (ESI, Fig. S4 and S5†).⁷

The second required building block towards bottle brush copolymers is a polymer containing an amine end group (Scheme 5). Monotelechelic PS was polymerized using ATRP



Scheme 4 ROMP of CE-*p*Cpd, **12**, and photo-isomerization at 395 nm.

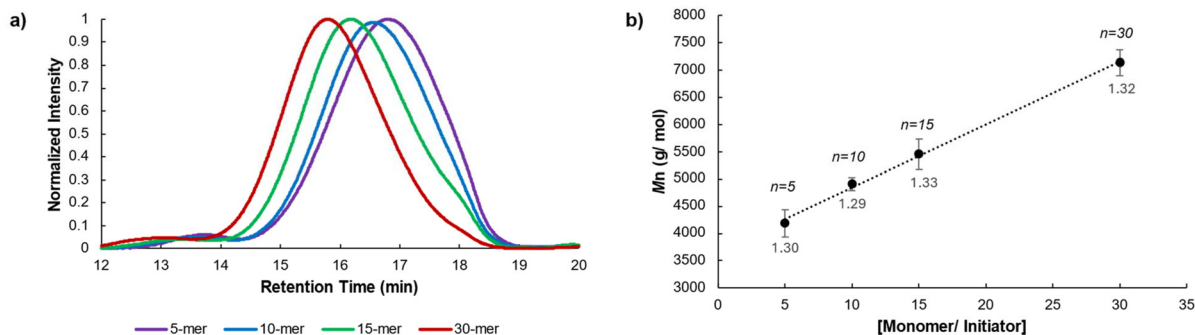
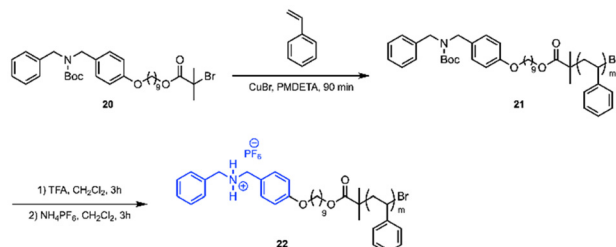


Fig. 1 (a) Molecular weight distribution of polymers **13a–d** (GPC in THF). (b) Dependence of M_n as measured by GPC of polymers **13a–d** on the $[M]/[I]$ ratio. Here, **13a**, $n = 5$, **13b**, $n = 10$, **13c**, $n = 15$, and **13d**, $n = 30$. Dispersity values of the respective polymers are denoted in the plot.

Table 1 GPC data and optical characterization of CE-PPVs

PPV	[M/I]	M_n , Calc. ^a	M_n , GPC ^b	M_n , NMR ^c	D	Yield %	Abs. $\lambda_{\max}$ ^d	Em. $\lambda_{\max}$ ^d
13a	5	3035	4200	3035	1.30	97	361	481
13b	10	5809	4900	6483	1.29	96	353	483
13c	15	8783	5500	9357	1.33	85	349	481
13d	30 ^e	17 402	7150	—	1.32	83	347	482
14	10- <i>trans</i>	5809	6400	—	1.40	Quant.	441	482
15	Diblock ^e	8164	29 400	—	1.26	87	408	516

^a M_n values were calculated based on the targeted degree of polymerization. ^b M_n GPC values were determined against poly(styrene) standards. The mobile phase was THF and the detector was UV-Vis. ^c The crown-ether protons of the CE-PPV were integrated against the isopropoxy proton of the end-group. ^d Measurements were done in dilute solutions of chloroform. ^e Feed ratio was too large for integration of signals.

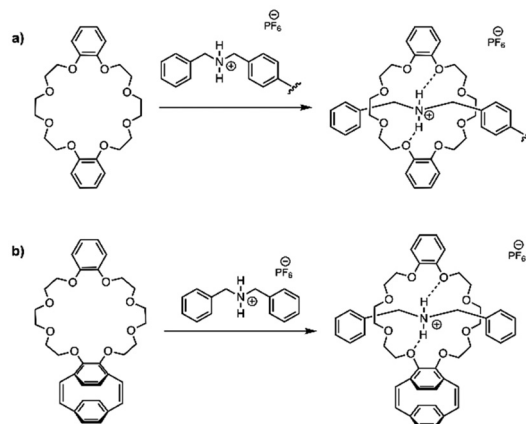
**Scheme 5** Synthesis of telechelic PS-DBA⁺, 22.

initiator **20** to yield polymer **21**.^{21,30} The amine end-group was boc-protected during the polymerization due to the presence of an amine causing uncontrolled polymerization behavior.¹⁷ Trifluoroacetic acid was used to deprotect the amine and then hexafluorophosphate was added to install a non-coordinating counter-ion for the creation of the ammonium chain-end, **22**.

ATRP reached 40% conversion in four hours and was terminated to prevent any deviation from first-order kinetics.³⁵ Aliquots of the polymerization were taken every 30 minutes under an argon atmosphere. The M_n of the aliquots, analyzed by GPC, increased with time to give monomodal polymers with narrow dispersities. The semilogarithmic plot showed that ATRP progressed with first-order kinetics, which indicates a living polymerization (ESI, Fig. S6†).

Self-assembly

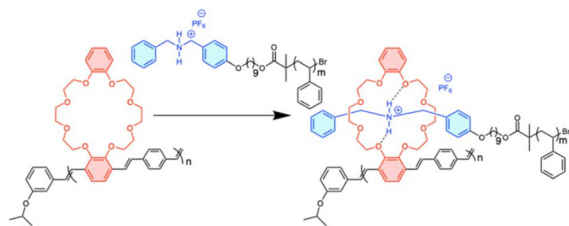
Small molecule assemblies. Dibenzo-24-crown-8 (DB24C8) and dibenzylammonium salt (DBA⁺) are known to assemble spontaneously in aprotic solvents with an association constant (K_a) of $1.7 \times 10^3 \text{ M}^{-1}$ in 1 : 1 chloroform/acetonitrile.²⁴ We first assembled commercially available DB24C8 and polymer **22**, PS-DBA⁺ (Scheme 6a) and observed characteristic complexation using ¹H NMR spectroscopy (ESI, Fig. S7†). Upon addition of excess PS-DBA⁺, a new signal at $\delta = 4.10$ ppm was observed that corresponds to “free” dibenzylammonium salt. Next, the ability of the small molecule host to form a pseudorotaxane was analyzed by complexing CE-*p*Cpd, compound **10**, with DBA⁺ in a 1 to 1 ratio (Scheme 6b). The characteristic methylene peaks of the crown-ether appeared between $\delta = 3.52$ and 4.16 ppm, and the benzylic peaks of the dibenzylamine salt appears at $\delta = 4.12$ ppm. The complexed methylene peaks

**Scheme 6** Pseudorotaxane formation. (a) The host is commercially available DB24C8 and the guest is PS-DBA⁺, **22**. (b) The host is CE-*p*Cpd, **12**, and the guest is commercially available DBA⁺.

appeared at $\delta = 4.28$, 4.63, and 4.94 ppm. The signal at $\delta = 4.08$ ppm corresponds to the salt (ESI, Fig. S8†).

Bottlebrush copolymer assembly. After examining the small molecule assemblies, the self-assembly of the polymeric units was investigated (Scheme 7, and Fig. 2). The guest, PS-DBA⁺ (**22**), was titrated into the host, CE-PPV (**13b**), to form the targeted polypseudorotaxane. The host-guest complex self-assembled in a 1 : 1 stoichiometric equivalence ratio (based on MRUs) in a solution of 1 : 1 chloroform and acetonitrile, chosen to fully solubilize the cationic salt. The complexed benzylic protons appeared at $\delta = 4.16$ to 4.39 ppm and the complexed crown-ether protons appeared from $\delta = 3.28$ to 3.42 ppm. New signals at $\delta = 2.78$ and 2.55 ppm represent the uncomplexed and complexed acidic ammonium cation (Fig. 2).³⁶ Upon addition of excess triethylamine, the ammonium cation was deprotonated, and the crown-ether complexation dethreaded.¹⁷ The complexed ammonium peaks disappeared and the benzylic protons of the dibenzyl amine appeared at $\delta = 3.68$ ppm (ESI, Fig. S9†). The polymeric bottlebrush is, therefore, pH responsive.

Due to the overlapping and broad peaks of the polymers, association constant (K_a) was not successfully calculated through ¹H NMR spectroscopy, so, isothermal titration calorimetry (ITC) using 1 : 1 CHCl₃/CH₃CN as the solvent was per-



Scheme 7 Bottlebrush copolymer assembly. The host is CE-PPV, **13b**, and the guest is PS-PBA⁺, **22**.

formed. PS-DBA⁺ (**22**) was titrated into CE-PPV (**13b**) and the heat of dilution of three blanks was subtracted from the measurement. The blanks were: solvent titrated into solvent, PS-DBA⁺ titrated into solvent, and solvent titrated into CE-PPV. The host solution had a concentration of 0.105 mM and the guest solution of 0.085 mM. The K_a was determined by a single-site binding model as $9.305 \times 10^4 \text{ M}^{-1} \pm 1.14 \times 10^4 \text{ M}^{-1}$ and the stoichiometry ratio (n) was found to be 1.28 ± 0.09 , which is similar to the 1:1 complexation seen in the small molecule counterparts (ESI, Fig. S10[†]). Please note that 10 equivalents of PS-DBA⁺ (**22**) were titrated into 1 equivalent of CE-PPV (**13b**), based on having a 10-mer host polymer with 10 CE binding sites. The polymeric units associated a magnitude of order stronger than their small molecule counterparts ($1.7 \times 10^3 \text{ M}^{-1}$).²⁴ We hypothesize that this is due to the increased

π -stacking in the conjugated PPV system compared to the reported small molecule complexes.

The changes in the hydrodynamic radius (R_h) between CE-PPV (**13b**) and the assembled CE-PPV-PS-DBA⁺ were characterized *via* dynamic light scattering (DLS) (Fig. 3a). The CE-PPV had an R_h of 1.5 nm with a narrow size distribution, whereas the CE-PPV-PS-DBA⁺ had a mean R_h of 2.8 nm, with a wide size distribution. Since the pseudorotaxane was designed as a bottlebrush copolymer, there would be a high local concentration of tethered chains forced to extend away from the polymer backbone, resulting in a larger R_h and wider size distribution. The assembly was analyzed by GPC, showing a decrease in elution time and an increase in dispersity (CE-PPV $D = 1.29$, PS-DBA⁺ $D = 1.04$ and for CE-PPV-PS-DBA⁺ $D = 1.36$). This change in dispersity and retention time may indicate that a larger aggregate than the homopolymers was formed, which is most likely the bottlebrush copolymer (Fig. 3b).²¹ It should be noted that the CE-PPV is a rigid-rod polymer while the PS-DBA⁺ is coiled. The bottlebrush would have characteristics of both: a more coiled character than CE-PPV while being more rigid than the PS-DBA⁺.

Optical data of the CE-PPV (**13b**), and the bottlebrush, CE-PPV-PS-DBA⁺ were collected in 1:1 CHCl₃/CH₃CN at a concentration of 0.46 μM . In this solvent mixture, compared to chloroform only, absorbance for the CE-PPV shifted from $\lambda_{\text{max}} = 353$ to 362 nm, and the emission shifted from $\lambda_{\text{max}} = 482$ to 506 nm.

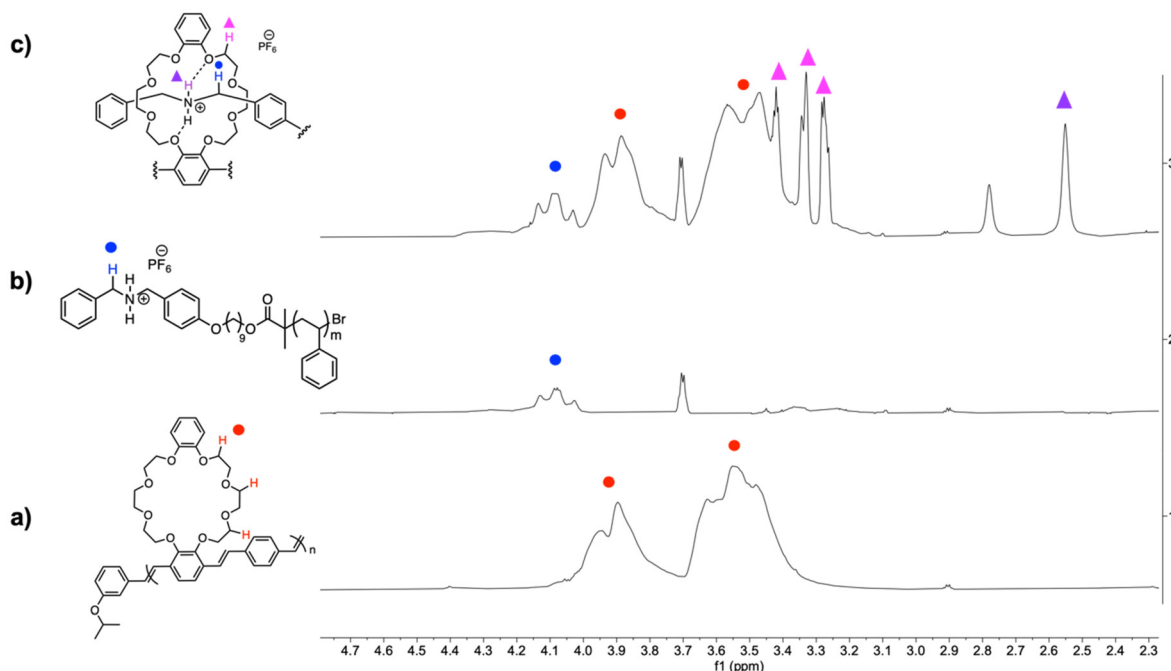


Fig. 2 ¹H NMR spectral overlay of 1.00 mM CE-PPV (**13b**) with PS-DBA⁺ (**22**) in 1:1 CDCl₃/CD₃CN showing the supramolecular interaction resonances of the DBA⁺ benzylic protons and CE protons. (a) Host-guest complex of CE-PPV and PS-DBA⁺ in an equimolar ratio, (b) host PS-DBA⁺ in 1:1 CDCl₃/CD₃CN, (c) guest CE-PPV in 1:1 CDCl₃/CD₃CN. The circles represent uncomplexed protons and the triangles represent complexed protons.

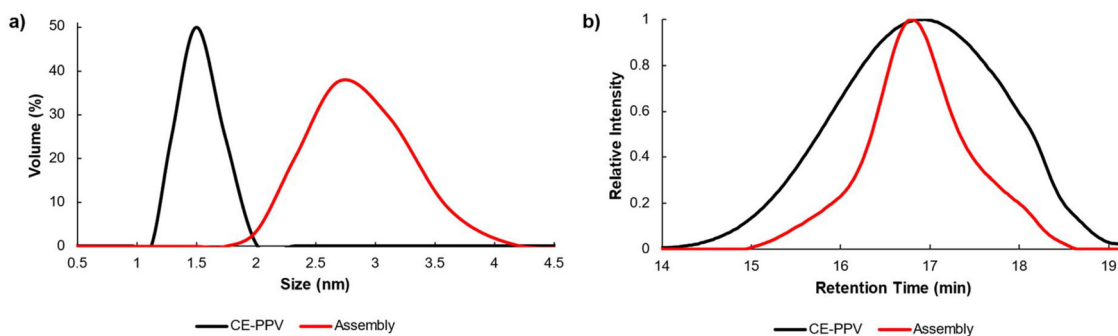


Fig. 3 (a) DLS in 1 : 1 $\text{CHCl}_3/\text{CH}_3\text{CN}$ and (b) GPC characterization in THF, against linear PS standards, of homopolymer CE-PPV (**13b**) (black) and the supramolecular bottlebrush CE-PPV-PS-DBA⁺ (red).

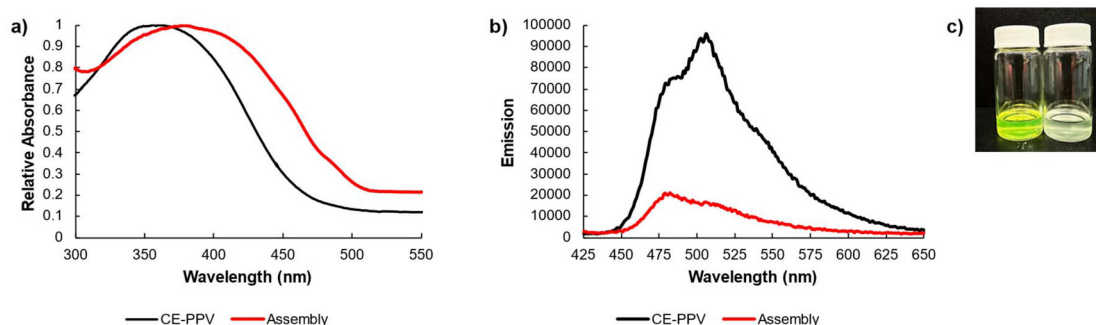


Fig. 4 (a) Absorbance spectra and (b) emission spectra of homopolymer CE-PPV (**13b**) (black) and the supramolecular bottlebrush CE-PPV-PS-DBA⁺ (red). (c) The CE-PPV has strong fluorescence (left) and the bottlebrush has quenched fluorescence (right).

Upon assembly, the absorbance red-shifted from $\lambda_{\text{max}} = 362$ nm to 379 nm, which is similar to reported shifts in the literature for host-guest complexes (Fig. 4a). The emission shifted from $\lambda_{\text{max}} = 506$ nm to 480 nm. The intensity saw a sharp, five-fold decrease in intensity from $\sim 100\,000$ to 20 000, indicating that a guest was encapsulated into the host along the backbone (Fig. 4b). When a host-guest complex is formed in a conjugated system, the analyte (**22**) induced aggregation of the system elicits a quenching response (Fig. 4c).^{37–40}

Wide-Angle X-Ray Scattering (WAXS) gave insights into the crystallinity and order of the assembled structure (Fig. 5). PPVs are known to have semi-crystalline domains that show a broad but strong scattering peak around $2\theta = 20^\circ$.⁶ The CE-PPV (**13b**) spectra shows this signature peak from $2\theta = 18$ to 21° . The Bragg's reflection at $2\theta = 22^\circ$ corresponds to the intra-backbone repeat units, *i.e.*, the crown-ether substituent. The sharper peak could suggest that the crown-ether increases crystallinity of the CE-PPV as compared to unsubstituted or alkoxy-substituted PPVs. This may be because the crown-ether adds bulk and restricts the rotational freedom of the polymer. Features at $2\theta = 30, 31$, and 37° ($d = 2.97, 2.88$, and 2.43 Å) indicate π -stacking. The assembled unit does not display any short-range order features, but the peak at $2\theta = 9.5^\circ$ corresponds to $d = 9.30$ Å, indicating long-range order. The reflection

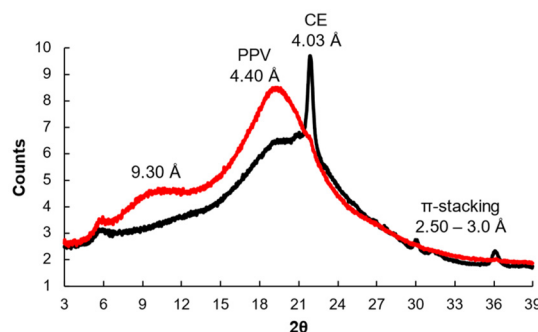


Fig. 5 WAXS diffractograms corresponding to homopolymer CE-PPV (**13b**) (black) and the supramolecular bottlebrush CE-PPV-PS-DBA⁺ (red).

at $2\theta = 5.5^\circ$ was from Kapton, which held the samples during the experiment.

Conclusions

This contribution describes a highly strained CE-*p*Cpd which, after living ROMP, yields CE-PPVs with a high degree of control over polymer properties. The living character of the

ROMP was determined by ^1H NMR spectroscopy, GPC, and with chain-extension experiments. The *cis-trans*-CE-PPVs were photo-isomerized to afford the conjugated all-*trans*-isomer. PS-DBA⁺ was synthesized using ATRP with control over molecular weights and dispersities. Brush copolymers were formed *via* the host-guest driven assembly of CE-PPV and PS-DBA⁺. The supramolecular bottlebrush is optically active, pH responsive, and semi-crystalline. This work depicts the first example of backbone-functionalized PPVs synthesized through ROMP and provides a platform to develop complex macromolecular architectures and supramolecular materials for applications in chemical sensing, optoelectronics, fluorescent imaging, and cross-linking.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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