

Complexation of Poly(phenylenevinylene) Precursors and Monomers by Cucurbituril Hosts

Yonghua Ling and Angel E. Kaifer*

Center for Supramolecular Science and Department of Chemistry, University of Miami, Coral Gables, Florida 33124-0431

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The formation of highly stable inclusion complexes between the host cucurbit [7]uril (CB7) and the dicationic guests bis(diethylsulfonium)-*p*-xylylene (**1²⁺**) and bis(tetrahydrothiophenium)-*p*-xylylene (**2²⁺**) was demonstrated by mass spectrometric, NMR and UV-vis spectroscopic data. Although the inclusion complexes did not undergo Wessling polymerization, the monomers can be pre-polymerized to the polyelectrolyte stage and subsequently exposed to CB7 in aqueous solution. The CB7-treated polyelectrolyte developed conjugation more readily and at much lower temperatures than the untreated polyelectrolyte to yield poly(phenylenevinylene) (PPV). The formation of external complexes between CB7 and the cationic branches of the polyelectrolyte favored the cleavage of the branches. CB7 was also found to form a stable complex with diethyl sulfide (Et₂S), the product of the elimination reaction that converts the polyelectrolyte to PPV. In contrast, the smaller analogue, the cucurbit [6]uril host (CB6) did not have any effect on the polyelectrolyte-to-PPV conversion. The CB7-treated polyelectrolyte showed enhanced luminescence both in solution and in precursor polymer films. Et₂S@CB7 inclusion complexes located around the polymer chains seem to form a hydrophobic shell, which effectively protects the PPV chains from quenchers, such as vapor-phase dinitrotoluene molecules.

Introduction

The family of the cucurbit[n]uril hosts has been the focus of considerable research interest in the past few years.^{1,2} The isolation by Kim and co-workers of cucurbit[7]uril (CB7) and cucurbit[8]uril (CB8) has opened up many research avenues that were not accessible with the smaller cavity analogue, cucurbit[6]uril (CB6).³ Among the semiconducting organic polymers, poly(phenylenevinylene) (PPV) has attracted considerable attention, with continuously expanding applications to a number of relevant new technologies, such as organic light-emitting devices (OLEDs).^{4–7} Because of our interest in the host chemistry of cucurbiturils, we started work on the complexation by CB7 of two dicationic xylylene monomers that can be utilized as precursors in the preparation of PPV. These two monomers (see Figure 1 for structures) are bis(diethylsulfonium)-*p*-xylylene (**1²⁺**) and bis(tetrahydrothiophenium)-*p*-xylylene (**2²⁺**). Our studies on the CB7 complexation of these two compounds led us to investigate the interactions between polymeric PPV chains and cucur-

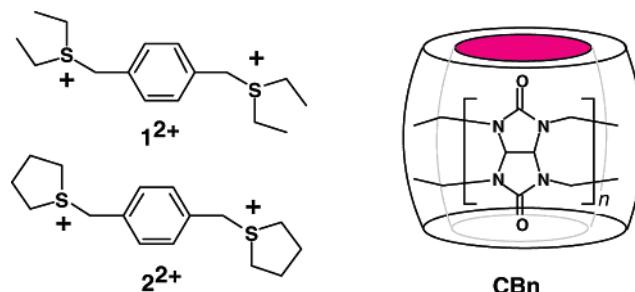


Figure 1. Structures of the monomer guests and cucurbit[n]uril hosts surveyed in this work.

bituril hosts. Here, we report the preliminary results of this work.

Experimental Section

Materials. All reagents were used as received, without further purification. Tetrahydrothiophene (99%), ethyl sulfide (98%), glycoluril, and 2,4-dinitrotoluene (97%) were purchased from Aldrich. α,α' -Dibromo-*p*-xylylene (>98% GC) was obtained from Fluka. Paraformaldehyde was purchased from Eastman.

Synthesis of *p*-Xylylene Sulfonium Salts and Cucurbit[n]-uril. These reagents were synthesized following previously reported procedures.^{8,9}

Synthesis of PPV. A 0.2 M monomer solution (5.0 mL) was reacted with an equimolar quantity of sodium hydroxide at 0 °C under rigorous anaerobic conditions. A highly viscous, clear solution was obtained after the reaction was quenched with 1 M HCl to

- * To whom correspondence should be addressed. E-mail: akaifer@miami.edu.
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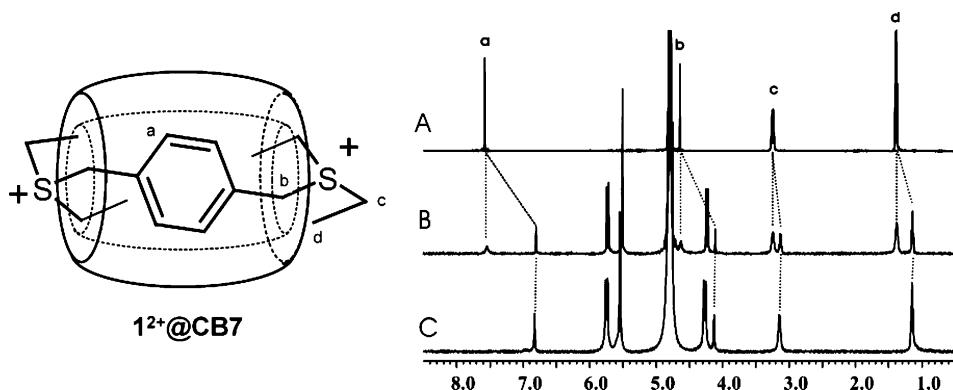


Figure 2. ^1H NMR spectra (500 MHz, 0.1 M NaCl/D₂O) of **1²⁺** in the absence (A) and in the presence of 0.5 equiv (B) and 1.2 equiv (C) of CB7. The proposed structure for the CB7-**1²⁺** complex is shown at the left.

slightly acidic (pH \sim 6) conditions. Dialysis can be used to separate the polymer from low molecular weight byproducts. However, a more convenient approach to purify the polyelectrolyte involved addition of the reaction mixture to a large excess of acetone which caused precipitation of the polyelectrolyte, while lower molecular weight species remained in solution. A web-like white precipitate formed instantly and was left under rapid stirring for about 15–20 min. The polyelectrolyte was filtered out and dried under vacuum for about 20 min and then carefully weighed out. The purified polyelectrolyte can be cut into smaller pieces, which can be easily used to prepare polymer solutions for quantitative studies. NMR spectroscopy was used to study the complexation effects. Polyelectrolyte films containing varying amounts of CB7 were cast on quartz slides and heated in an inert atmosphere. Extreme care was placed to ensure that these films were always prepared from a fixed volume of solution containing a fixed concentration of polyelectrolyte, but some degree of variability on film thickness was unavoidable. The resulting films were thus expected to contain the same amount of polyelectrolyte and variable amounts of CB7 host. The optical properties of these films were studied by UV-vis and fluorescent spectroscopy.

Instrumentation. UV-vis spectra were obtained on a Shimadzu UV-2101 PC UV-vis scanning spectrophotometer using quartz slides (Hellma Worldwide, spectral range 200–2500 nm). Fluorescent spectra were recorded on a Spex Fluoromax spectrofluorometer. Infrared spectra were obtained on a Perkin-Elmer 2000 FT-IR instrument. ^1H NMR spectra were obtained on a Bruker 500 MHz spectrometer using 5 mm o.d. tubes.

Results and Discussion

The formation of an inclusion complex between monomer **1²⁺** and CB7 is clearly evident from the ^1H NMR spectra of mixtures of both compounds in aqueous solution (0.1 M NaCl/D₂O). Addition of 1.2 equiv of CB7 to a solution of the monomer leads to a pronounced upfield shift ($\Delta\delta = 0.75$ ppm) of its phenylene protons (Figure 2). The benzylic methylene protons also shift upfield ($\Delta\delta = 0.48$ ppm) and so do both the methyl (~ 0.1 ppm) and methylene (0.22 ppm) protons on the four terminal ethyl groups covalently attached to the sulfur atoms. The pronounced upfield shifts experienced by the phenylene and benzylic methylene protons on the guest molecule are consistent with the formation of an inclusion complex in which the phenylene residue is centered inside the CB7 cavity, with the carbonyl portals interacting with the positively charged sulfur atoms via ion-dipole

forces.^{10,11} The upfield shifts for the terminal methyl and methylene protons are unusual and suggest that the diethyl groups may be folded toward the cavity.¹⁰ Inclusion complexation of **2²⁺** by CB7 also gives rise to a pronounced upfield shift of the phenylene and benzylic methylene protons, but the protons on the tetrahydrothiophenium groups actually shift downfield, as anticipated for protons held outside the portals of the host.¹⁰ Complexes of both monomers exhibit slow exchange in the NMR time scale; that is, proton signals corresponding to both the free guest and the complex were simultaneously observed in the presence of less than 1.0 equiv of CB7 (Figure 2B).

The complexation can also be monitored using UV-vis absorption spectroscopy. Monomer **1²⁺** shows an absorption band at 226 nm that is depressed upon addition of CB7. UV-vis titrations of the monomer with increasing concentrations of the host give rise to plots composed of two straight lines intersecting at a well-defined breaking point. These plots reveal quantitative complexation at the absolute concentration levels used in these experiments and indicate that the association equilibrium constant (K) is higher than 10^6 M^{-1} , in agreement with previous observations made by our group on the binding constants between CB7 and structurally related guests.¹¹ In order to obtain the K value between guest **1²⁺** and CB7 we performed UV-vis titrations in the presence of an excess of a nonabsorbing reference guest, hexylenediamine, in 50 mM sodium acetate (pH 4.74). Under these conditions, Isaacs and co-workers have measured a K value of $8.97 \times 10^7 \text{ M}^{-1}$ for complexation of hexylenediamine by the CB7 host.¹² Fitting of the absorbance data to the two simultaneous, competing 1:1 binding equilibria leads to $K = 4.0 \times 10^{10} \text{ M}^{-1}$ for the association of **1²⁺** and CB7 (Supporting Information). The formation of stable inclusion complexes between CB7 and guests **1²⁺** and **2²⁺** was also evident from MALDI-TOF mass spectrometric data (Supporting Information).

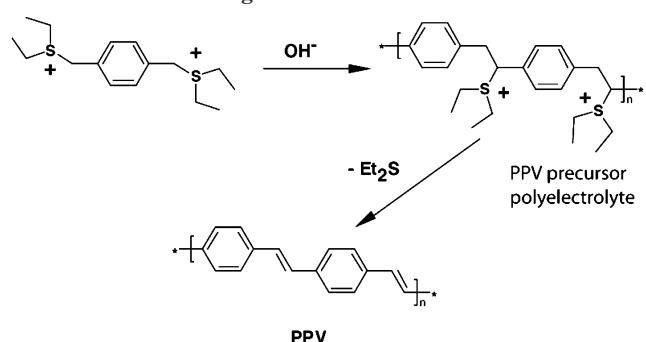
Monomers **1²⁺** and **2²⁺** are both useful for the preparation of PPV by the so-called Wessling route.¹³ In this approach polymerization of the monomer in basic solution leads to the formation of a water-soluble cationic polyelectrolyte,

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Scheme 1. Wessling Route to PPV from Monomer 1^{2+} 

which can be isolated by precipitation with acetone. Upon heating, this polyelectrolyte is converted into PPV by an elimination reaction (Scheme 1).

Since our data clearly establish that dication 1^{2+} and dication 2^{2+} form highly stable inclusion complexes with CB7, we set out to investigate whether these inclusion complexes will undergo Wessling polymerization to yield CB7-based polypseudorotaxanes. So far, all our attempts to drive the polymerization from the inclusion complexes have failed. This finding can be rationalized as a result of the stabilization of the sulfonium groups by the carbonyl portals of CB7 in the inclusion complex. In a different group of experiments, CB7 was added to a solution containing the cationic polyelectrolyte prepared by base treatment of 1^{2+} (see Scheme 1). This procedure led to intriguing results. First, upon addition of CB7, the broad proton NMR resonances corresponding to the polyelectrolyte disappear (Supporting Information). While this experimental finding is not completely understood at this point, we believe that the disappearance of the peaks is due to extensive broadening related to host exchange processes and slow tumbling of the polymer chains when the CB7 hosts interact with the polyelectrolyte chains. In contrast to this, the smaller cavity analogue CB6 had no effect on the ^1H NMR signals of the polyelectrolyte (Supporting Information). Furthermore, we also investigated directly the binding interactions between CB7 and CB6 with diethylsulfide (Et₂S), which is the major product from the elimination reaction in which the cationic polyelectrolyte is converted into neutral PPV (Scheme 1). We found that CB7 forms a moderately stable inclusion complex with Et₂S. The complexation between CB7 and Et₂S is a slow exchange process in the NMR time scale, and the association equilibrium constant (K) is determined to be 1500 M^{-1} (Supporting Information). Therefore, the presence of CB7 should favor the elimination of Et₂S by product stabilization via inclusion complexation. However, the smaller cavity analogue CB6 does not interact with Et₂S. On the basis of these findings, we conclude that the CB7 hosts bind to the cationic sulfonium branches of the polyelectrolyte. Our NMR spectroscopic data on the $1^{2+}@\text{CB7}$ inclusion complex (vide supra) suggested that the diethyl sulfonium groups are encapsulated inside CB7 (Figure 2A). It is thus quite reasonable to assume that when the polyelectrolyte in solution is exposed to CB7, the host molecules “dock” on the polyelectrolyte’s sulfonium sidearms, driven by ion-dipole forces and hydrophobic interactions. On the other hand, the smaller cavity of CB6 cannot bind the sulfonium branches

and thus exerts no effect on the proton NMR resonances of the polyelectrolyte. We also found that the larger host cucurbit[8]uril (CB8) does not form a stable inclusion complex with Et₂S.

To further explore the interaction of CB7 with the sulfonium branches we investigated the changes induced by CB7 on the absorption and emission spectra of the polyelectrolyte. The addition of CB7 to the polyelectrolyte solution causes a slight red shift of the maximum absorbance band at 230 nm (see Supporting Information), which can be explained by the interaction of the carbonyl portals of CB7 with the positively charged sulfur atoms. A similar red shift was also observed previously when CB7 was added to monomer 1^{2+} (Supporting Information). Figure 3A shows that the addition of CB7 host to an aqueous solution of the polyelectrolyte leads to an enhancement of the observed luminescence intensity. No red shift of the emission bands was observed, however, suggesting that the interaction of CB7 with the polyelectrolyte in aqueous solution does not lead to a significant development of conjugated, unsaturated polymer segments. From the above experimental evidence, we conclude that the CB7 host binds to the sulfonium branches and forms external complexes around the polymer chain, and most of these CB7 bound branches remain covalently attached to the main polymer chain. These external complexes create a hydrophobic microenvironment, which protects the polyelectrolyte chains from interchain interactions and quenchers.

Precursor polymer films were prepared under mild heating ($60\text{ }^\circ\text{C}$) to efficiently remove the solvent. Some sulfonium branches may be removed from the polymer chain during this process. Films prepared from CB7-treated polyelectrolyte solutions exhibit interesting electronic absorption features. Specifically, we found that the exposure of the polyelectrolyte to CB7 leads to films that have a more intense absorption band at 328 nm. In fact, the maximum absorbance at this wavelength increases linearly with the concentration of CB7 utilized in these experiments (Figure 4). This spectroscopic band is associated to the presence of *trans*-stilbene units along the polymer chains.¹⁴ Therefore, we conclude that the interaction of the polyelectrolyte with CB7 facilitates the elimination reaction, leading to polymeric chains that have increased *trans*-stilbene character. The *trans*-stilbene content is linearly related to the amount of CB7 present in the films. CB7 does not seem to enhance the polymer’s degree of conjugation, since no red shift of the maximum absorbance band was observed. In other words, the detachment of the CB7-bound sulfonium branches is facilitated as compared to the same process in the absence of CB7. Thus, treatment with CB7 promotes the formation of stilbene units along the chain, but these stilbene units are not necessarily conjugated.

The influence of the external CB7 complexes on the kinetics of the elimination reaction was also investigated by NMR experiments at variable temperature. These experiments were carried out with polyelectrolyte solutions under $60\text{ }^\circ\text{C}$, when the phenyl signals of the polyelectrolyte are

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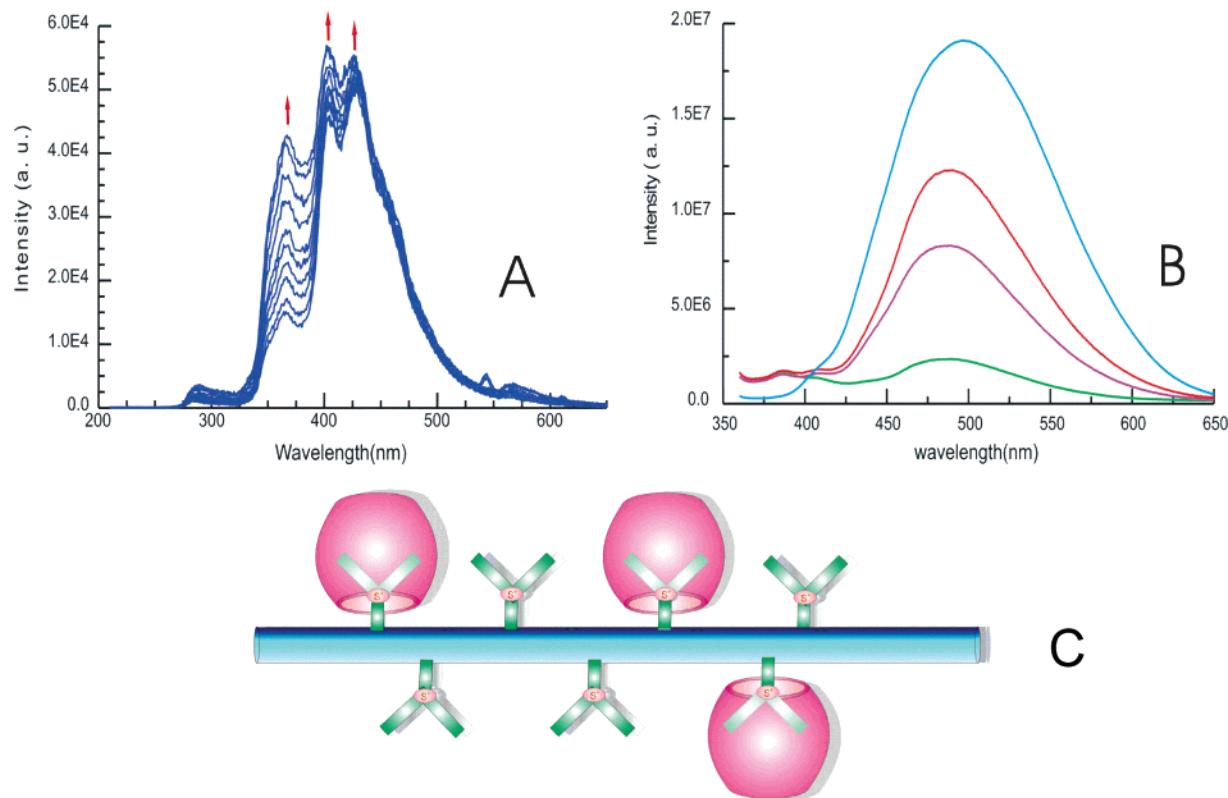


Figure 3. (A) Luminescence spectra of 0.125% aqueous solution of polyelectrolyte in the presence of increasing CB7 concentrations (from 3.35×10^{-4} M to 2.95×10^{-3} M). (B) Luminescence spectra of precursor films containing 0.0 (green), 0.2 (purple), 0.5 equiv (red), and 0.8 equiv (blue) of CB7. All films were prepared using the same volume of solution containing a fixed concentration of polyelectrolyte (0.05%) and variable CB7 concentrations. All films are dried under vacuum at 55 °C overnight to effectively remove the solvent. Excitation wavelength = 350 nm. (C) Schematic drawing of external complexes formed between the CB7 host and the cationic sulfonium branches.

still well-defined in the presence of 0.6 equiv of CB7. The progress of the elimination reaction can be followed by monitoring the relative concentration of the products Et₂S or Et₂S@CB7. The phenyl proton signals of the polyelectrolyte at the same concentration were used as a reference. The integrated peak areas measured for the Et₂S protons were compared to those of the phenyl protons in order to quantify the concentration of Et₂S present in the solution. Figure 5A shows that the amount of Et₂S produced from the CB7-treated polyelectrolyte was 7.3-fold larger than the amount of Et₂S produced from untreated polyelectrolyte after identical reaction times. In the solution treated with CB7, most Et₂S molecules exist as Et₂S@CB7 inclusion complexes. This finding together with our previous data strongly supports that CB7 favors the elimination reaction via product (Et₂S) stabilization. CB7 accelerates the elimination of the sulfonium branches and the kinetics of the reaction from precursor polyelectrolyte to conjugated PPV.

It is well-known that the Et₂S elimination reaction (and the development of conjugation along the polymer chains) is assisted by heating the films at temperatures above 150 °C. We found that the presence of CB7 in the films substantially favors Et₂S elimination, leading to fully conjugated PPV films at much lower temperatures than those needed to complete the elimination reaction in films not containing any CB7¹⁵ (see Figure 6). Also CB7-treated polymer films contain more chromophores than plain films.

The CB7 host, however, did not extend the conjugation length of the polymer. The PPV films used here had shorter conjugation lengths compared to those used in other studies,¹⁵ since we did not dialyze the polyelectrolyte to remove oligomers.

One of the more important properties of PPV films is their strong luminescence. Initially we investigated the effect of variable CB7 concentrations on the luminescence of films prepared from polyelectrolyte solutions. Before any heat treatment, these films are predominantly constituted by polyelectrolyte chains having a large number of positively charged branches (Scheme 1). Exposure of the polyelectrolyte in solution to CB7 leads to films with enhanced luminescence, a finding which is consistent with our previous luminescence data obtained in the solution phase (Figure 3). In the CB7-treated precursor films, most CB7-bound sulfonium branches are still attached to the polymer chain and form a hydrophobic microenvironment around the polymer chain which results in pronounced luminescence enhancement. However, our experimental results reveal that the emission from CB7-modified, heat-treated PPV films show lower luminescence intensity than that obtained from CB7-free PPV films under the same experimental conditions (Supporting Information). This finding is not fully understood at this point but it might be related to the Et₂S@CB7 inclusion complexes located close to the PPV chain. After detachment from the polymer chain, the Et₂S@CB7 complexes still retain their position close to the polymer in the film. Some of the excitons might get “captured” by these

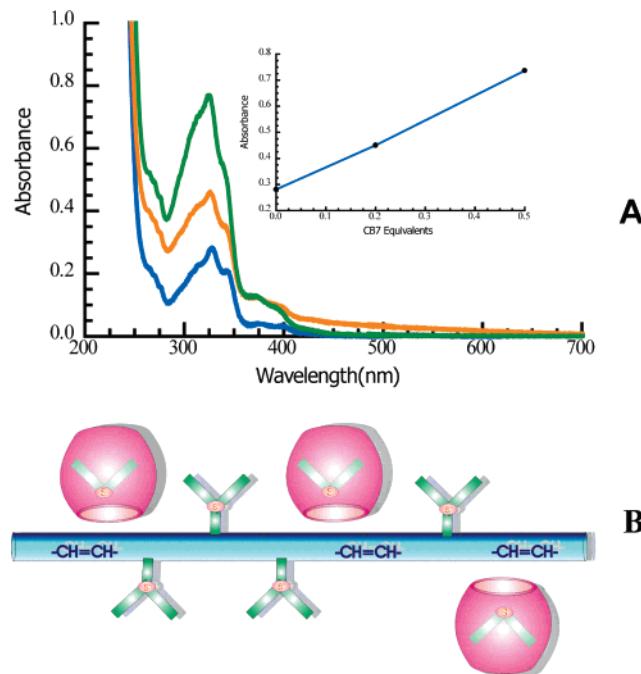


Figure 4. (A) Room-temperature electronic absorption spectra of prepolymer films containing 0.0 (blue), 0.2 (orange), and 0.5 equiv (green) of CB7. The inset shows the dependence of the absorbance at 328 nm on the content of CB7 in the films. All films were prepared using the same volume of solution containing a fixed concentration of polyelectrolyte (0.5%) and variable CB7 concentrations. (B) Schematic drawing of *trans*-stilbene units formed on the polymer chain.

complexes as they hop along the PPV chain. Further work will be necessary to clarify this point. In addition, the luminescent properties of PPV films can be utilized to sense the presence of electron acceptor compounds through electron-transfer quenching mechanisms. Recently, Swager and co-workers have demonstrated the use of PPV films derivatized with hydrophobic groups as fluorescent sensors for dinitrotoluene (DNT) in the gas phase.^{16,17} Exposure of these hydrophobic PPV films to DNT vapor effectively quenches the PPV luminescence. We found that the luminescence of our PPV films is also quenched effectively by DNT. However, the CB7-containing PPV films only experience minor quenching when exposed to DNT in the gas phase (Figure 7). This finding suggests that, after their detachment from the main polymer chain, most Et₂S@CB7 complexes remain around the PPV chain, forming a shell around the polymer and largely preventing the excitons on the polymer chains from interacting with the electron acceptor DNT molecules. Since our experimental conditions do not exclude the presence of some oligomers, CB7 complexation of the two chain ends may also play a minor role in our data. In contrast to this, CB8-modified PPV films undergo quenching when exposed to similar vapor concentrations of DNT. These experimental data are intriguing, but consistent with our hypothesis that CB7 forms external complexes with the sulfonium sidearms. CB6 and CB8 do not form a stable complex with Et₂S, as discussed before. While CB6 has a cavity too small to interact with Et₂S or any other polymer

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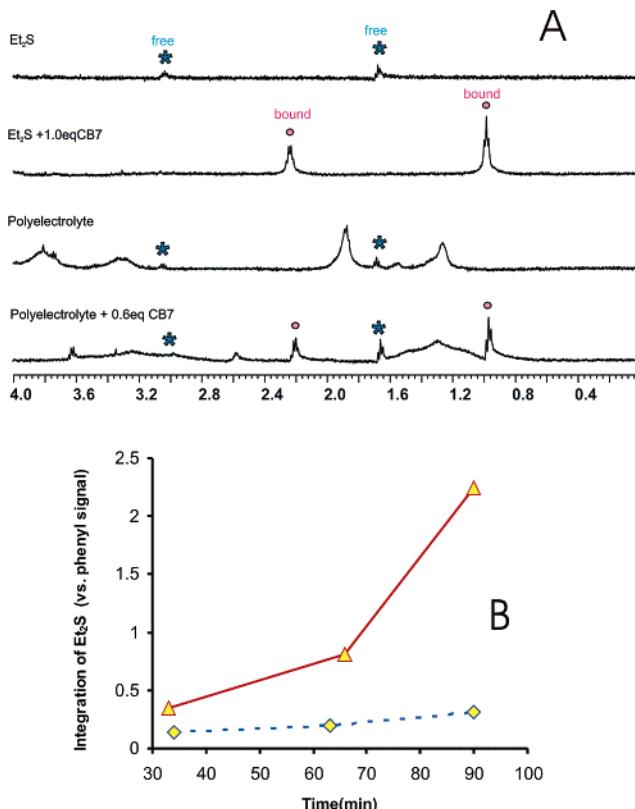


Figure 5. (A) 60 °C NMR spectra (300 MHz, D₂O) showing evidence of Et₂S inclusion complexation by CB7 (two top spectra) and evidence for the presence of the Et₂S@CB7 inclusion complex when the polyelectrolyte (PPV precursor) is exposed to CB7 (two bottom spectra). The amount of Et₂S released from the CB7 treated polyelectrolyte is 7.3 times more than that from the polyelectrolyte under the same experimental conditions. (B) Comparison of the amount of Et₂S released in polyelectrolyte solutions at 60 °C containing no CB7 (dashed line) and 0.8 equiv of CB7 (solid line) at different reaction times.

components, this is not the case with CB8. However, CB8 does not bind Et₂S, but it could interact with the cationic polyelectrolyte in nonspecific ways or, perhaps, by threading onto the polymer chain.¹⁸ The luminescence of CB8-treated PPV films is quenched by DNT, but higher concentrations of quencher are needed to attain a given level of quenching as compared to untreated PPV films. The very low solubility of CB8 in aqueous media—lower than those for CB6 and CB7—seriously limits the investigation of this host as an additive. The addition of CB8 host also results in the disappearance of the polyelectrolyte's ¹H NMR resonances. It is reasonable to assume that the larger-cavity CB8 could thread onto the polymer chain¹⁸ and cause its proton resonances to disappear. If this is the case, an alternative mechanism for CB8-modified PPV luminescence quenching by DNT vapor could be proposed. The threaded CB8 hosts may become excellent binding sites for the electron acceptor DNT molecules as they could develop charge transfer interactions^{19,20} with the electron donor *trans*-stilbene units of the PPV chain and thus facilitate the electron-transfer process between PPV and DNT inside its cavity.

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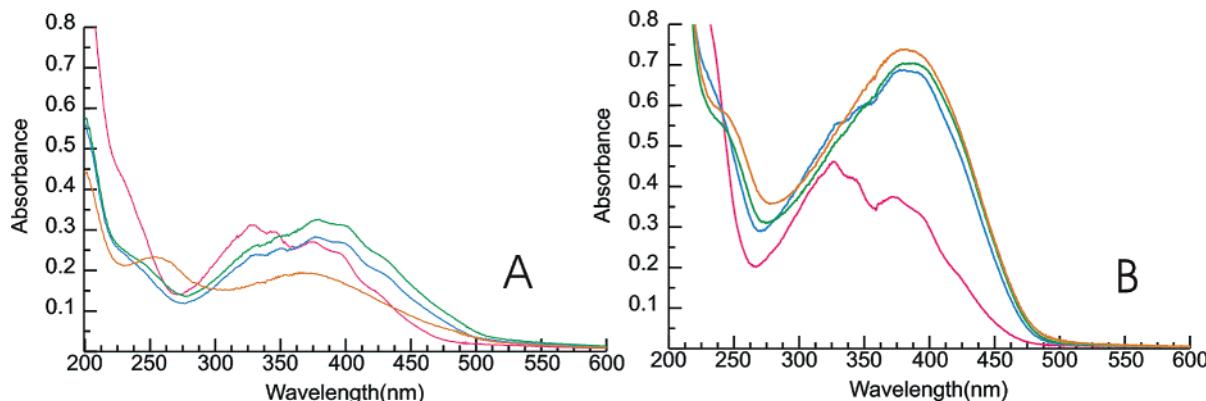


Figure 6. Electronic absorption spectra of (A) the polymer film and (B) the polymer film treated with 0.5 equiv of CB7 after heating in argon at 65 °C, 110 °C, 155 °C, and 205 °C, respectively. All films were prepared using the same volume of solution containing a fixed concentration of polyelectrolyte (0.16%) and variable CB7 concentrations.

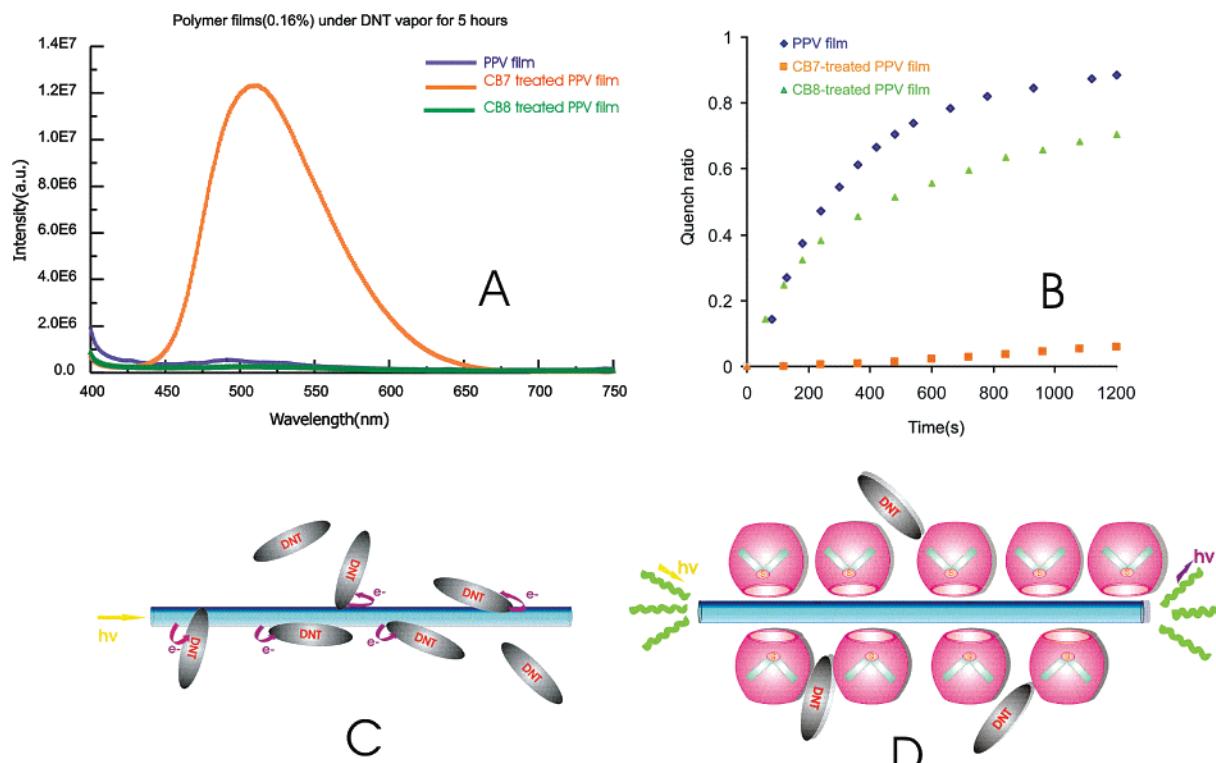


Figure 7. (A) Emission spectra of PPV (blue), CB7-modified PPV (red), and CB8-modified PPV films (green) exposed to saturated DNT vapor at room temperature for 5 h. (B) PPV (blue), CB7-modified PPV (red), and CB8-modified PPV (green) luminescence quenching as a function of exposure time to DNT vapor. DNT(g) was present at its vapor pressure at room temperature. (C) Schematic drawing showing the quenching by DNT molecules of the excitons on the PPV chains. (D) Schematic drawing showing the protection from quenching by DNT molecules afforded by Et₂S@CB7 complexes located around the PPV chains.

In summary, we have shown that CB7 forms highly stable inclusion complexes with monomers **1**²⁺ and **2**²⁺, but the inclusion complexes do not undergo Wessling polymerization. However, the precursor polyelectrolyte obtained by base treatment of **1**²⁺ interacts with the CB7 host, leading to CB7-containing materials that easily undergo elimination of their diethylsulfonium branches, developing conjugated PPV much faster at lower temperatures. The collectivity of the experimental data presented here can be rationalized by the formation of external complexes between CB7 and the sulfonium branches on the polyelectrolyte, followed by an elimination reaction, which is favored through product stabilization in the Et₂S@CB7 inclusion complexes. We are

currently investigating other properties and applications of PPV polymeric chains protected by cucurbituril macrocycles.

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Supporting Information Available: Additional data as mentioned in the text (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.