Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 48 (2007) 4613–4617

Tetrahedron Letters

A pseudopolyrotaxane consisting in PPV threaded in multiple cucurbiturils

Avelino Corma,* Hermenegildo Garcia* and Pedro Montes-Navajas

Instituto de Tecnologia Quimica, Universidad Politecnica de Valencia, Av. De los Naranjos s/n, 46022, Valencia, Spain

Received 8 February 2007; revised 17 April 2007; accepted 23 April 2007
Available online 27 April 2007

Abstract—*p*-Phenylenedimethylene-1,1′-bis(tetrahydrothiophen-1-ium) dibromide ($PBTHBr_2$), one of the possible monomers of poly(*p*-phenylenevinylene) (PPV), forms a very stable complex with cucurbiturils (CBs) of the appropriate internal diameter as assessed by ^{1}H NMR. Using $PBTH^{2+}$@CB[7] as starting material, the corresponding PPV@CB[7], a pseudopolyrotaxane in which phenylenevinylene units are inserted in CB[7]s, was obtained by condensation with NaOH and thermal treatment at 200 °C. Considering that many applications of PPV derive from luminescence, observation of a strong emission for PPV@CB[7] with a lifetime somewhat shorter than the pure polymer makes also this material useful for applications in nanotechnology.

Given the shape, choice of internal diameters and specific properties as hosts of cucurbiturils (CBs), there is much current interest in exploiting the ability of these capsules to incorporate organic guests.[1,2] CBs have a pumpkin-like shape, with larger diameter at the centre than at the rims of the molecule. In addition, the presence of carbonyl groups at the portals controls the ingress to the host and also the stability of the resulting complexes. The electrostatic interaction with these carbonyls is the reason why CBs form adducts with inorganic cations and positively charged nitrogenated heterocyclic compounds such as viologens[3,4] and rhodamine 6G.[5,6]

In a recent related precedent to our work, it has been reported that *p*-phenylenedimethylene-1,1′-bis(tetrahydrothiophen-1-ium) hexafluorophosphate [$PBTH(PF_6)_2$] forms a stable complex with CB[7] but polymerisation of this complex was not achieved.[7] In the present work we also provide data in agreement with the $PBTH^{2+}$ complexation with CB[6]–CB[8] and, more importantly, we have effected the polymerization of the encapsulated monomer to form poly(*p*-phenylenevinylene) (PPV) threaded in CBs.

PPV is one of the most widely studied conducting polymers that has application in nanotechnology as an active component for photovoltaic devices and electroluminescent diodes.[8,9] Drawbacks associated with PPV, such as the lack of solubility, difficult processability and poor stability due to degradative oxidation of the C–C double bonds, could be overcome by embedding the polymer into an appropriate host that improves processability at the same time that it increases the stability of the polymer. While remarkable complexation of CB with organic cations have been reported,[4,5] examples of the encapsulation of a neutral polymer inserted in many CBs (a supramolecular pseudopolyrotaxane) are much more rare.[10] One of the major points of this contribution is to show that it is possible to perform chemical reactions with the supramolecular entity consisting in an organic cation incorporated tightly inside CBs.

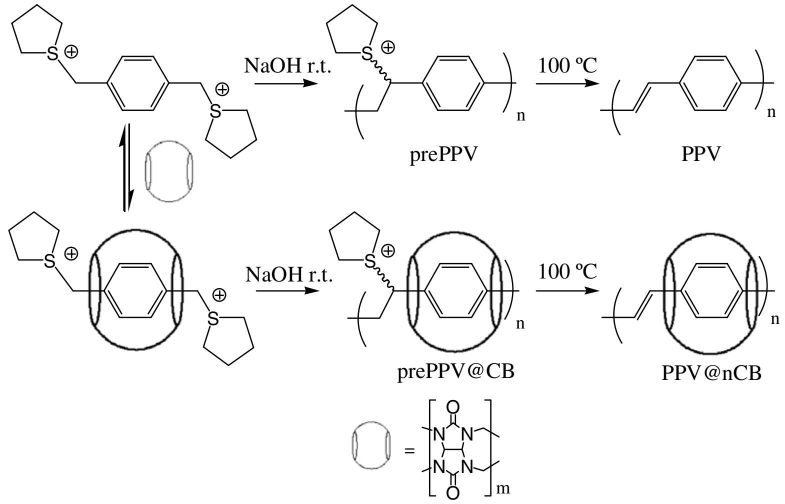
A convenient way to obtain PPV consists in the polymerisation of $PBTH^{2+}$ dibromide under basic conditions, followed by thermal elimination of the thiophenium groups.[8,9] We anticipate that $PBTH^{2+}$@CB complexes can be used to form the corresponding polymer. Scheme 1 presents the expected process for the formation of PPV threaded in CBs.

In order to demonstrate the feasibility of the processes described in Scheme 1, we started studying by ^{1}H NMR the complexation between CB[5]–[8] and $PBTHBr_2$. Figure 1 shows some selected ^{1}H NMR

Keywords: Host–guest complexes; Organic capsules; Wrestling polymerization; Conducting polymers.

* Corresponding authors. Tel.: +34 963877807; fax: +34 963877809; e-mail: hgarcia@qim.upv.es

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.04.112



Scheme 1. Formation of PPV by polymerisation of $PBTH^{2+}$ or PBTH@CB under basic conditions.

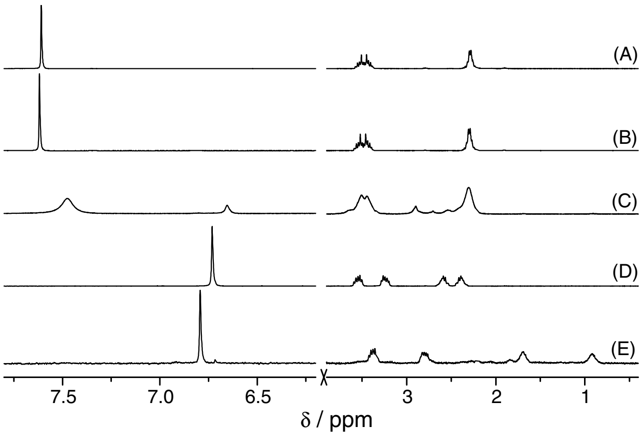


Figure 1. Relevant regions of the ^1H NMR spectra recorded in D_2O for $PBTHBr_2$ in the absence (A) and in the presence of excess of CB[5] (B), CB[6] (C), CB[7] (D) and CB[8] (E).

spectra to illustrate the changes observed in the $PBTH^{2+}$ signals upon addition of CBs.

As it can be seen there (spectrum A in Fig. 1), the ^1H NMR spectrum of $PBTH^{2+}$ has a singlet at 7.6 ppm corresponding to the four equivalent aromatic protons, while the tetrahydrothiophenium ring appears as two sets of multiplets corresponding to the α and β protons of the pentacyclic ring in axial and equatorial configuration. When the spectrum of $PBTH^{2+}$ is recorded in the same solvent in the presence of an excess of CB[5] (Fig. 1, spectrum B), no changes are observed. In contrast to this, the chemical shifts of the aromatic as well as the tetrahydrothiophenium protons undergo considerable changes when the ^1H NMR spectrum is recorded in the presence of CB[7] and CB[8]. These changes in the chemical shift are a firm evidence that complexation has occurred and $PBTH^{2+}$ is hosted inside the organic capsule. A careful inspection of the chemical shifts reveals significant differences between the final δ values measured for $PBTH^{2+}$ protons in excess of CB[7] and CB[8], probably indicating variations in the location of the $PBTH^{2+}$ inside the CB host with respect to the carbonyl groups of the portals. Our results totally agree with those of $PBTH(PF_6)_2$ in CB[7]. In the case of CB[6], an intermediate situation between CB[5] and CB[7] was observed and together with a remarkable broadening of the ^1H NMR signals (indicating the occurrence of dynamic equilibrium of the species in the ^1H NMR time scale) the two sets of signals characteristic of uncomplexed $PBTH^{2+}$ and CB[6] complexed $PBTH^{2+}$ were simultaneously recorded (5:1 proportion).

Molecular mechanic MM2 calculations predict that encapsulation of $PBTH^{2+}$ in CB[5] is not feasible due to spatial restrictions, while the driving force for complexation is favourable in the case of CB[6]–[8]. From this modelling, it is also predicted that the organic capsules distort their round conformation to an oval shape to better accommodate the organic guest. The molecular models agree with the ^1H NMR study (see Supplementary Fig. S1).

Estimations of the binding constants (K_b) for the complexation of $PBTH^{2+}$ with CB[6]–CB[8] were attempted by titration of a 10^{-4} M solution of $PBTHBr_2$ in D_2O with the corresponding CBs following the evolution of uncomplexed and complexed $PBTH^{2+}$ by ^1H NMR. However, the high values of the K_b precluded an accurate estimation since essentially all the CBs were stoichiometrically complexed, thus indicating that K_b values are higher than 10^5 M^{-1} (see Supplementary data for titration data). For analogous bis(diethylsulfonium)-*p*-xylylene encapsulated in CB[7] the binding constant has been estimated to be 4×10^{10} M^{-1} and it is reasonable to assume that $PBTH^{2+}$ (the cyclic analogue of the bis(diethylsulfonium) group) should exhibit a similar binding constant.[7]

Having provided spectroscopic evidence in support of the formation of host–guest $PBTH^{2+}$@CB[6], $PBTH^{2+}$@CB[7] and $PBTH^{2+}$@CB[8], the polymerisation of these supramolecular entities was attempted. Polymerisation requires NaOH that effects deprotonation of one acidic benzylic proton to form the ylide at the α-position of the sulfonium group.[8] Upon addition of an aqueous NaOH solution to $PBTH^{2+}$@CB in water, a yellow color gradually develops until a maximum intensity is reached. This color change could be compatible with the formation of a PPV prepolymer as indicated in Scheme 1. After the neutralisation of the resulting polymeric suspension in water, the mixture was dialysed in order to remove small molecules and any CB left in the reaction. The resulting sample was cast on glass and heated at 200 °C to promote tetrahydrothiophene elimination and formation of the PPV film as indicated in Scheme 1.

Surprisingly, the three samples evolved differently depending on the size of the CB host. Thus, in the case of $PBTH^{2+}$@CB[6], which was the sample with the most intense yellow color, spectroscopic hallmarks of CB[6] in Raman and IR spectroscopy were not detected in the resulting film that, however, corresponds to the pure PPV. Apparently, during the treatment with NaOH in water, decomplexation occurred. On the other extreme, spectroscopic characterisation of the almost colorless film upon treatment of $PBTH^{2+}$@CB[8] indicates that PPV is not formed with sufficient quality.

In sharp contrast with the previous two hosts, in the case of CB[7], following the two-step procedure consisting in room temperature treatment with a base and subsequent heating, the successful formation of PPV polymer encapsulated in multiple CB[7] units (PPV@nCB[7]) could be convincingly demonstrated by UV–vis, IR and Raman spectra. These spectra of PPV@nCB[7] film match remarkably well with those of pure PPV prepared analogously in the absence of CB, except for the presence in IR and Raman spectroscopy of the extra peaks corresponding to CB[7]. Figures 2–4 firmly show the formation of PPV when the $PBTH^{2+}$@CB[7] complex is used as monomer. Chemical analysis based on the N content (5.75%) have established that the resulting PPV@nCB[7] has a CB[7] capsule every six phenylene-vinylene units.

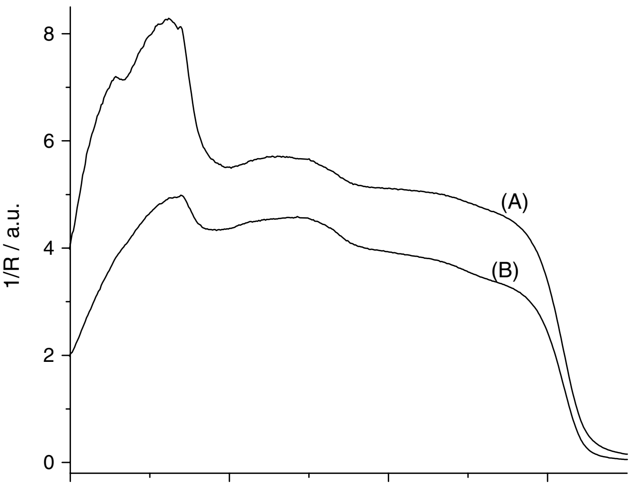


Figure 2. Diffuse reflectance UV–vis spectra (plotted as the inverse of reflectance) of PPV (A) and PPV@nCB[7] films (B).

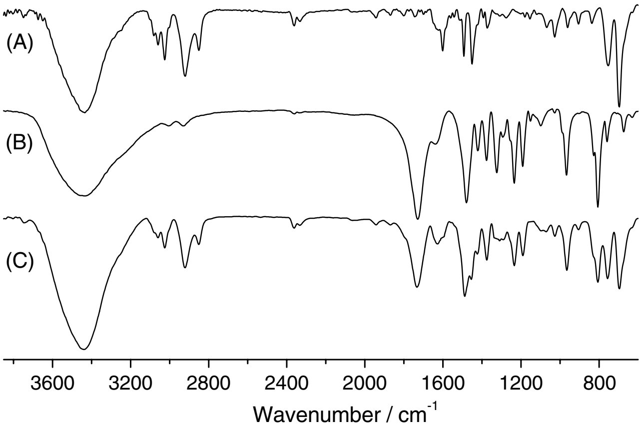


Figure 3. Room temperature FT-IR spectra of PPV (A), CB[7] (B) and PPV@nCB[7] (C).

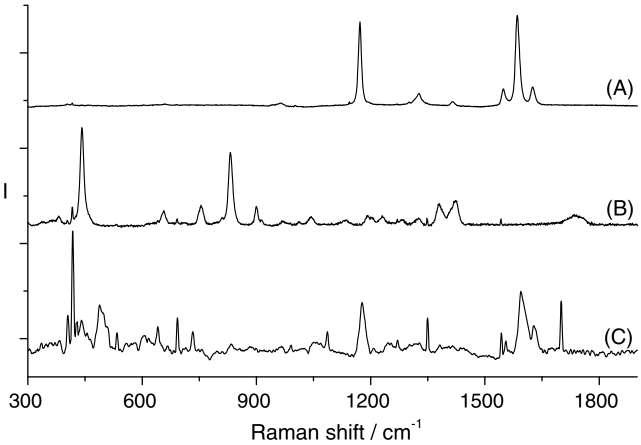


Figure 4. Raman spectra of PPV (A), CB[7] (B) and PPV@nCB[7] (C).

The fact that PPV is successfully formed starting with the host–guest $PBTH^{2+}$@CB[7] complex as monomer does not guarantee that PPV is threaded in a multitude of CB[7] forming a pseudopolyrotaxane. In fact, it may occur that upon the action of the base when the proton is abstracted and the ylide cation is generated as reaction intermediate, de-threading occurs forming free CB[7] and uncomplexed ylide. It has to be noted that the ylide intermediate will lose the net positive charge in one of the terminus but still have a positive tetrahydrothiophenium terminus that could maintain the stability of the complex for a period sufficiently long to undergo condensation with another monomer. This intermolecular step involving one sulphur ylide attacking a complexed sulfonium group should also be disfavourable with respect to the situation involving uncomplexed intermediates since nucleophilic attack requires a geometrical specificity in the approaching direction of the nucleophile towards the leaving group for the reaction to occur.

This, together with the different stability of the ylides@CB complexes, may be the reasons why polymerisations of $PBTH^{2+}$@CB[6] (de-threading of the ylide) and PBTH^{2+}@CB[8] (probably influence by the steric hindrance to the nucleophilic attack) fail. Only in the case of PBTH^{2+}@CB[7] there is an optimal combination of ylide complex stability and spatial requirements for the nucleophilic attack.

On the other hand, the fact that the polymer is formed with the PBTH^{2+}@CB[7] complex does not ensure that the resulting polymer is also threaded. We noticed, however, that the PPV@nCB[7] sample that was characterised spectroscopically, was previously submitted to dialysis to remove any residual amount of CB[7] that could have been left uncomplexed during the synthesis of PPV@nCB[7] as was the case of PBTH^{2+}@CB[6]. In fact, we performed a blank control in which a 10^{-3} M aqueous solution of CB[7] was submitted to the same dialysis treatment, the concentration of CB[7] inside the membrane being reduced by over 90% of the initial concentration. Therefore, the presence of CB[7] in the sample strongly suggests complexation with the polymer.

To specifically address threading of CB[7] through PPV, we performed an in situ ^{1}H NMR study of the room temperature polymerisation process (Fig. 5). Upon addition of the base, the upfield shielded signal characteristic of the aromatic protons of complexed PBTH^{2+} inside CB[7] is maintained decreasing progressively in intensity over time, while concomitantly two new broad signals around this peak appear (see arrows in spectra of Fig. 5). The chemical shifts of these new signals clearly establish that they are aromatic protons inside CB[7] and their broadness is compatible with their assignment to a polymer. Noteworthy is the fact that the symmetry of the PBTH^{2+} monomer leading to a singlet in the aromatic region is lost when the saturated tetrahydrothiophenium polymer is formed. The possibility that during the formation of the prePPV precursor, CB[7] dethreads from the phenylene ring and rebinds to the tetrahydrothiophenium lateral chain seems unlikely based on the presence of CB in the final PPV@nCB and on the chemical shifts of the ^{1}H NMR spectra after the room temperature NaOH treatment to form prePPV@nCB[7] (Fig. 5, spectrum E).

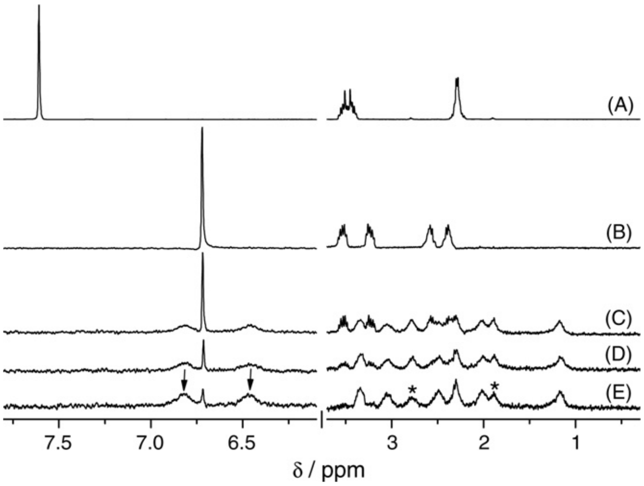
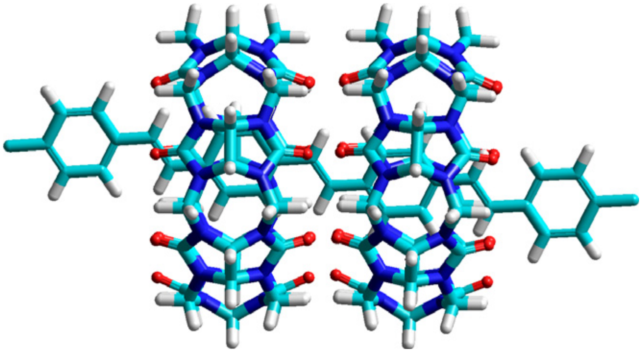


Figure 5. Relevant regions of the ^{1}H NMR spectra of free PBTH^{2+} monomer (A), PBTH^{2+}@CB[7] complex (B) and the previous sample 5 (C), 15 (D) and 24 (E) hours after addition of a 0.4 M aqueous solution of NaOH.

Moreover, in the aliphatic region changes of the tetrahydrothiophenium protons compatible with the gradual formation of the polymer are also observed, that is, decrease in intensity of the signals corresponding to the encapsulated monomer and the appearance of new broad signals at different chemical shifts due to the polymeric intermediate. Furthermore, the signals of tetrahydrothiophene (the by-product arising from the intermolecular polymer growth) are also observed at 1.9 and 2.8 ppm (see asterisks in Fig. 5).

The above spectroscopic data firmly establish that after polymerisation, the sample consists in a pseudopolyrotaxane in which phenylenevinylene units are inserted in a CB[7] host. Importantly, previous attemps to form PPV@nCB[7] by reacting PBTH@CB[7] have met with failure.[7] Scheme 2 shows a molecular modelling of the pseudopolyrotaxane PPV@nCB[7].

Given that electroluminescence is one of the main applications of PPV, it is of interest to determine if PPV@nCB[7] also exhibits intense fluorescent emission. For this reason, we recorded the emission spectrum of PPV@nCB[7] upon excitation at 400 nm, whereby an intense fluorescence coincident with that of pristine PPV



Scheme 2. Molecular model at MM2 level of PPV@CB[7].

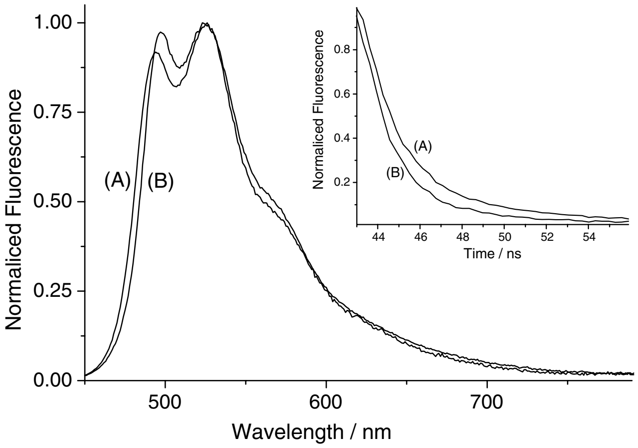


Figure 6. Fluorescence spectra ($\lambda_{exc} = 400$ nm) of PPV (A) and PPV@nCB[7] (B). The inset shows the temporal profile of the emission measured at 500 nm for PPV (A) and PPV@nCB[7] (B) films.

films was observed. Figure 6 shows the emission spectrum in which the characteristic fine structure of the fluorescence is observed. Time-resolved measurements establish however that the lifetime of fluorescence is considerably shorter (0.47 ns) for PPV@nCB[7] than the emission of pure PPV films (1.23 ns). This change in the emission lifetime may be a reflection of the confinement of phenylene units inside CB[7] capsules. The observation of this intense photoluminescence suggests that PPV@CB[7] should exhibit the same remarkable properties as those reported for PPV.

References and notes

1. Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870.
2. Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630.
3. Ong, W.; Kaifer, A. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2164–2167.
4. Moon, K.; Grindstaff, J.; Sobransingh, D.; Kaifer Angel, E. *Angew. Chem.* **2004**, *43*, 5496–5499.
5. Mohanty, J.; Nau, W. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3750–3754.
6. Marquez, C.; Nau, W. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3155–3160.
7. Ling, Y.; Kaifer, A. *Chem. Mater.* **2006**, *18*, 5944–5949.
8. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
9. Friend, R. *Nature* **2006**, *441*, 37.
10. Ooya, T.; Inoue, D.; Choi, H. S.; Kobayashi, Y.; Loethen, S.; Thompson, D. H.; Ko, Y. H.; Kim, K.; Yui, N. *Org. Lett.* **2006**, *8*, 3159–3162.