

# Synthesis and Photochemical Properties of Poly(2,5-dimethoxy-*p*-phenylenevinylene) Hosted in the Intergallery Spaces of Montmorillonite

Mercedes Alvaro, Belén Ferrer, Hermenegildo Garcia,\* and Encarna Peris

*Instituto de Tecnología Química and Department of Chemistry, Universidad Politécnica de Valencia, 46022 Valencia, Spain*

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Poly(2,5-dimethoxy-*p*-phenylenevinylene) (dMeOPPV) has been formed in the intergallery spacing of a montmorillonite by introducing the (2,5-dimethoxy-1,4-phenylene)bis(methylene-*S*-tetrahydrothiophenium) monomer by ion exchange, increasing the basicity of the solid aluminosilicate with Cs<sup>+</sup> and subsequent heating at 200 °C. dMeOPPV@montmorillonite was characterized by optical spectroscopy, FT-IR spectroscopy, solid-state <sup>13</sup>C NMR, photoluminescence, and chemical analysis. All the data are compatible with that reported in the literature for pure dMeOPPV. The dMeOPPV polymer incorporated inside montmorillonite exhibits a green light emission which makes the organic polymer very attractive for its application in polymer light-emitting diodes (PLEDs). The new polymeric material can be submitted to laser irradiation (laser power, 10 mJ pulse<sup>-1</sup>) under oxygen without decomposition.

## Introduction

Recently we have reported the preparation of poly(*p*-phenylenevinylene) (PPV) encapsulated within faujasite zeolites.<sup>1</sup> PPV is an electroluminescent polymer that becomes gradually degraded by oxidation of its C=C double bonds, thereby losing its properties.<sup>2–5</sup> A remarkable effect of the encapsulation inside zeolites was an increase of its chemical and thermal stability.<sup>1</sup> This stability was simply proved by exposing to the open air the PPV-containing zeolite sample to numerous laser shots without observing decomposition of the polymer. Identical conditions using no encapsulated PPV led to prompt degradation of the polymer. It is a general phenomenon frequently observed in supramolecular zeolite host–guest chemistry that the stability of the incorporated guests increases dramatically upon encapsulation.<sup>6</sup> This effect is particularly notable in those cases in which there is a tight fit between the guest within the inert, rigid zeolite framework. PPV encapsulated within faujasites exhibited a weak electroluminescence, and, therefore, it is a promising system with potential application for polymer light-emitting diodes (PLEDs).<sup>1</sup>

As a continuation of this previous work, we wanted to expand the study to a PPV derivative containing two methoxy groups in relative para positions. Dialkoxy-substituted PPV having long alkyl chains have been even more studied than the parent unsubstituted PPV.<sup>7,8</sup> The presence of two alkoxy substituents increases the efficiency of the electroluminescence. In addition, a long alkyl chain on the alkoxy group renders the PPV polymer somewhat soluble in organic solvents and facilitates its processability.<sup>8</sup>

In the present work we report the failure to incorporate the monomeric precursor of poly(2,5-dimethoxy-*p*-phenylenevinylene) (dMeOPPV) inside Cs<sup>+</sup>- and K<sup>+</sup>-exchanged faujasites and the successful synthesis of this conducting dMeOPPV polymer hosted in the intergallery regions of montmorillonite.

Zeolites and layered clays have in common that they are

crystalline aluminosilicates having a negatively charged framework and charge balancing alkali cations in the internal voids.<sup>9,10</sup> Both types of materials can host into the interior organic species.<sup>11–13</sup> The main difference between them is the topology of the accessible intracrystalline spaces. The geometry of the available space to adsorb organic species in layered clays, and specifically the montmorillonite used in the present work, is defined by 2D planes in the interlamellar spaces. In contrast to zeolites, where the micropores are rigid and undeformable, the distance between the montmorillonite layers can vary to adapt the size and volumes of the incorporated guest, giving rise to the phenomenon of swelling in which the interlayer distance increases depending on the solvent.<sup>11</sup>

Layered clays have also been widely used as hosts in supramolecular chemistry.<sup>11</sup> However, in contrast to zeolites, the adsorption capacity of clays is limited to highly polar guests or in highly polar solvents.<sup>14,15</sup> The Coulombic interaction between the layers and intergallery alkali metal ions is so strong that the layers are as close as possible and the empty free space available for adsorption of layered clays is negligible, although they can expand if the electrostatic forces are weakened and polar guests can be included in this way.

## Experimental Section

The monomer (2,5-dimethoxy-1,4-phenylene)bis(methylene-*S*-tetrahydrothiophenium) has been synthesized following the method employed in the literature.<sup>16</sup> A mixture of HCl (37%, 59 mL), formaldehyde (39%, 35 mL), 1,4-dimethoxybenzene (67.4 mL), and dioxane (100 mL) was stirred at 20 °C for 18 h. After this time, the mixture was heated at reflux temperature for 4 h. After cooling the sample, a solid precipitate appeared. The mixture was filtered, and the solid was washed with methanol. To a suspension of the solid in dry methanol (133 mL), tetrahydrothiophene (14 mL) was added. It was observed that the solid dissolved within 10 min and then the solution was heated at 50 °C for 17 h. After this time, dry acetone was added to the mixture and a solid precipitate appeared. The solution was then filtered under suction and dried.

\* To whom correspondence should be addressed. Phone: (+)34-963877807. Fax: (+)34-963879349. E-mail: hgarcia@qim.upv.es.

Incorporation of the monomer into montmorillonite was achieved by stirring an ethanol solution (20 mL) of the monomer (352 mg) with montmorillonite GADOR (previously dehydrated by heating at 250 °C under vacuum for 3 h; 1 g) for 6 h at 70 °C. After this time the sample was filtered and submitted to solid–liquid extraction with  $\text{CH}_2\text{Cl}_2$ .

Alkali-exchanged montmorillonite was obtained from the montmorillonite containing the monomer by ion exchange at room temperature using aqueous  $\text{CsAcO}$  solutions of 0.6 M concentration.

Polymerization of the monomer to form the polymer poly-(2,5-dimethoxy-*p*-phenylenevinylene) was accomplished by heating the solid in a tubular oven at 200 °C under reduced pressure for 24 h. The loading of the polymer was determined by combustion elemental analysis (C, N, H, and S) using a Fisons Analyzer.

Diffuse reflectance UV–visible spectra were recorded in a Cary 5 G spectrophotometer adapted with an integrating sphere using  $\text{BaSO}_4$  as reference. IR spectra were recorded in a Nicolet 710 nm spectrophotometer using a sealed greaseless cell adapted with CaF windows. Self-supported wafers of montmorillonite were obtained by compressing the powder at about 2 tons  $\text{cm}^2$ . Solid-state  $^{13}\text{C}$  NMR was recorded spinning the sample at 3 kHz at the magic angle in a Varian 400 MHz.

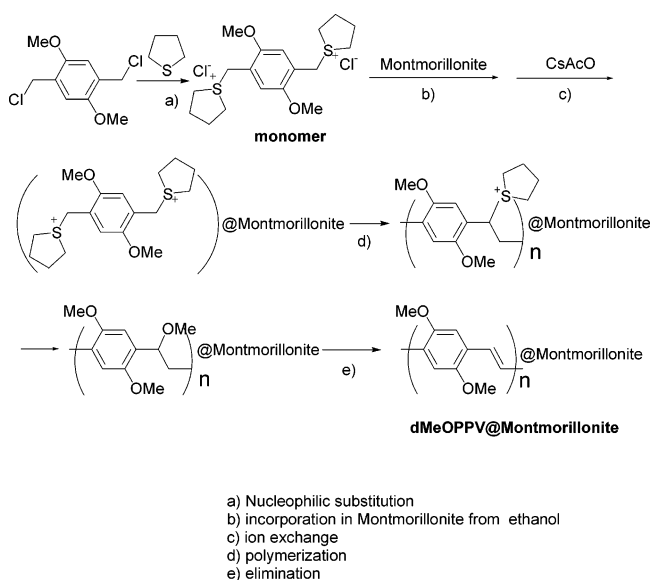
Photoluminescence spectra were recorded in an Edinburgh FS900 spectrophotometer having a solid sample accessory and Czerny Turner monochromators. Laser flash photolysis measurements were performed using the third harmonic (355 nm) frequency of a Surelite Nd:YAG laser as the excitation source. Signals from the photomultiplier tube were captured and digitalized by a Tektronix 2440 transient digitizer and transferred to a PC programmed in the LabView environment. Details of similar time-resolved diffuse reflectance systems have been described elsewhere.<sup>17</sup> The powders were placed in a  $3 \times 7$  mm<sup>2</sup> Suprasil quartz cuvette capped with septa, and the solids were purged with  $\text{N}_2$  before recording the spectra.

## Results and Discussion

In preliminary experiments we wanted to expand the synthetic procedure used for the preparation of PPV encapsulated in faujasites (PPV@zeolite) to its 2,5-dimethoxy derivative. 2,5-Dialkoxy derivatives of PPV are used in the construction of organic electroluminescent devices (PLEDs) even more frequently than parent PPV.<sup>18</sup> The reason for this is that the presence of two strong electron donor substituents such as the dialkoxy groups enhances considerably the ease of polaron generation through electron abstraction.<sup>19</sup> The difficulty of polaron formation is one of the main problems in the operation of PLEDs based on parent PPV, requiring the presence of a strong hole injection layer.<sup>20–24</sup> On the other hand, the use of large alkyl chains in the dialkoxy substituents has been used as a tool to increase the solubility of PPV, favoring the ease of polymer processability.

On the basis of the interest of 2,5-dialkoxy derivatives of PPV, we consider the possibility of incorporating the (2,5-dimethoxy-1,4-phenylene)bis(methylene-*S*-tetrahydrothiophenium) monomer and proceed to the polymerization using basic zeolites in a way parallel to that reported by us for PPV.<sup>1</sup> However, all the attempts to adsorb the bis(tetrahydrothiophenium) monomer met with failure and the faujasites (either Na–Y or Na–X) were recovered free from the organic dication. Adsorption was attempted at increasing temperatures, but at high temperatures the monomer reacted in the solution and a yellow gummy polymer was formed separately from the zeolite powder.

## SCHEME 1

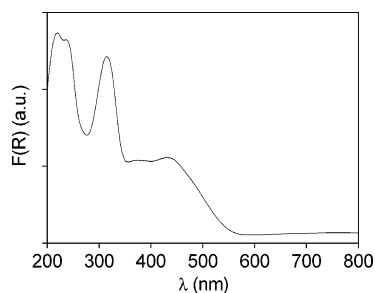


Chemical analyses revealed in all cases that the C and S content of the faujasites after the attempted incorporation was negligible. We interpreted this unsuccessful adsorption as due to the large molecular size of the 2,5-dialkoxy-substituted monomer compared to the unsubstituted one that precludes diffusion through the zeolite 0.74 nm micropores.

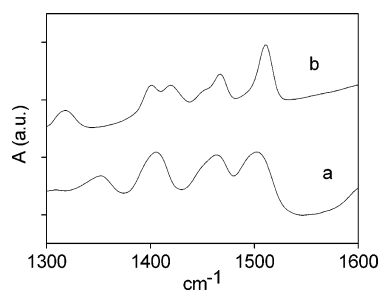
In view of the inability of large-pore zeolites to incorporate the 2,5-dialkoxy monomer, we moved to montmorillonites for which the interlamellar space will vary depending on the size of the adsorbed cation. As anticipated, incorporation of the monomer into montmorillonite was successfully achieved. Chemical analyses of the resulting montmorillonite indicates C and S contents of 9 and 1 wt %, corresponding to a 15% of the total ion exchange capability of the montmorillonite.

Subsequently, the montmorillonite containing 2,5-dimethoxyphenylene dication was ion exchanged with  $\text{CsAcO}$  to introduce some basicity in the solid, and the resulting dry powder was heated at 200 °C under vacuum to form the corresponding dMeOPPV. The progress of the polymerization can be visually observed for the change of the sample from white to an intense orange color. The actual synthetic procedure followed for the formation of dMeOPPV@montmorillonite is summarized in Scheme 1.

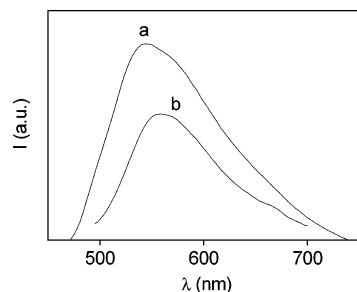
Formation of dMeOPPV@montmorillonite was confirmed by spectroscopic techniques. Diffuse reflectance UV–vis spectrum shows the presence of the characteristic absorption bands of dMeOPPV in the visible region at 442, 315, 218, and a shoulder at 238 nm (Figure 1). These absorption bands are coincident with that reported for pure dMeOPPV.<sup>8</sup> Figure 2 compares the IR spectrum of dMeOPPV@montmorillonite with that of an



**Figure 1.** Diffuse reflectance UV/Vis spectrum (plotted as the Kubelka–Munk function  $F(R)$ ) of dMeOPPV@montmorillonite.



**Figure 2.** Aromatic region of the FT-IR spectrum of an authentic sample of dMeOPPV polymer (a) and of the sample dMeOPPV@montmorillonite recorded at room temperature after outgassing the sample at 200 °C under  $10^{-2}$  Torr for 1 h (b).

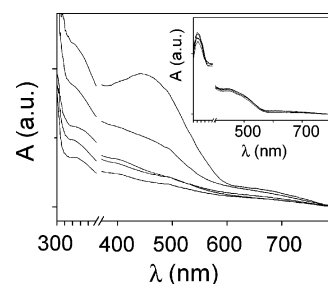


**Figure 3.** Room-temperature emission spectra of an authentic sample of dMeOPPV (a) and of the material dMeOPPV@montmorillonite (b) recorded upon 440 nm excitation under air atmosphere.

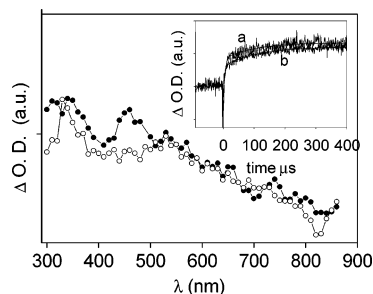
authentic sample of the pure polymer. As it can be seen there, the spectrum of the dMeOPPV@montmorillonite is coincident with that of the pure polymer particularly in the aromatic region, where all the following peaks are present in both spectra: 1502, 1453, 1405, and 1353  $\text{cm}^{-1}$ . The solid-state MAS  $^{13}\text{C}$  NMR spectrum of dMeOPPV@montmorillonite shows a signal at 57 ppm which could correspond to the  $\text{sp}^3$  carbons of the methoxy groups and a broad signal at 153 ppm corresponding to  $\text{sp}^2$  carbons characteristic for the structure of poly(phenylenevinylene). Figures 1 and 2 give information about the purity and the successful formation of the dMeOPPV polymer into the layers of the montmorillonite.

To assess that the incorporation of the monomer and subsequent polymerization process do not affect the crystalline structure of the montmorillonite, except by changing the intergallery spacing, we have recorded the X-ray diffractogram of the montmorillonite before and after polymerization. Both of them show the expected peaks, but the  $d_{100}$  peak shifts from  $2\theta = 6$  to 7 corresponding to an intergallery spacing of 6 and 12 Å, respectively. Then, we can conclude that the polymerization process has not changed the layered structure of the montmorillonite but only the distance between the layers.

We have measured the photophysical properties of dMeOPPV@montmorillonite. Figure 3 shows the photoluminescence spectrum of this sample upon excitation at 440 nm. The polymer dMeOPPV inside the montmorillonite presents an emission band with maximum at 555 nm which is 10 nm red-shifted with respect to that recorded for an authentic sample of polymer.<sup>18</sup> Pure PPV shows a characteristic structured emission band which is not present in the dMeOPPV polymer.<sup>1</sup> Then the introduction of the methoxy groups in the structure of the polymer causes the loss of this structured emission band. Both polymers, PPV and dMeOPPV, incorporated inside zeolites or montmorillonite present a photoluminescent spectrum with a maximum around 550 nm. This green light emission makes the organic polymers very attractive for its application in PLEDs.



**Figure 4.** Diffuse reflectance UV–visible spectra of a pure dMeOPPV film after 355 nm laser irradiation (10 mJ pulse $^{-1}$ ) for 0, 1, 1.5, 2, and 3 min at 1 Hz frequency. The inset shows the diffuse reflectance UV–visible spectra of the dMeOPPV@montmorillonite sample submitted to the same irradiation conditions.



**Figure 5.** Diffuse reflectance transient absorption spectra of the sample dMeOPPV@montmorillonite recorded under  $\text{N}_2$  (●) and  $\text{O}_2$  (○) atmosphere 1.4 ms after 355 nm laser excitation. The inset shows the transient signals monitored at 350 and 450 nm for the  $\text{N}_2$ -purged sample.

As it happens to the PPV polymer, its derivative dMeOPPV exhibits very low photostability in the presence of oxygen which is able to degrade the polymer. Moreover, laser irradiation of a pure dMeOPPV film causes the decomposition of the polymer, as it can be seen in Figure 4 from the disappearance of the characteristic absorption band of the polymer. When the dMeOPPV polymer was incorporated in the layers of montmorillonite, its stability increases remarkably. Thus, a film of the material dMeOPPV@montmorillonite can be submitted to laser irradiation (laser power 10 mJ pulse $^{-1}$ ) under oxygen without decomposition (see inset of Figure 4).

The photostability of dMeOPPV@montmorillonite also compares favorably with other closely related PPV derivatives that are more widely used than dMeOPPV itself. Thus, for instance, due to their better solubility and easier handling, alkoxy derivatives with longer alkyl chains (in contrast to methoxy group) are generally the derivatives of choice for application in PELDs. For this reason, we submitted also 2,5-bis(hexyloxy)-PPV (dHexOPPV) and 2,5-bis(3',7'-dimethyloctyloxy)PPV (d[dMeOc]OPPV) to the same photostability test, whereby, as expected, degradation basically followed the same pattern as was observed for dMeOPPV. This is not surprising considering that the main structural difference between dMeOPPV and the other alkoxy derivatives is the length of the alkyl chain rather than the core of the conducting polymer structure.

Once the remarkable photostability of dMeOPPV@montmorillonite was proved, we submitted a sample to laser flash photolysis to determine the nature of the photogenerated transients decaying in the sub-millisecond time scale. Figure 5 shows the diffuse reflectance transient absorption spectra recorded for this sample under  $\text{N}_2$  and  $\text{O}_2$  atmosphere 1.4 ms after 355 nm laser excitation. There were only minor differences between the transient spectra recorded under  $\text{N}_2$  or under  $\text{O}_2$ . Both spectra consist of a continuous absorption extending over



the entire wavelength range with the intensity decreasing gradually toward longer wavelengths.

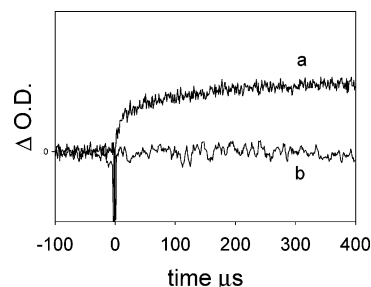
The temporal profiles of the signals monitored at different wavelengths were all coincident, suggesting that the spectra correspond to a single species (see inset of Figure 5). This species will not be quenched by O<sub>2</sub>, thereby the coincidence of the spectra recorded under purging N<sub>2</sub> or O<sub>2</sub>.

As it can be seen in the inset of Figure 5, all the signals show an intensity growth and do not decay even 5 ms after the laser pulse, the longest time scale available in our nanosecond setup. In addition to an instantaneous buildup of the signal in the monitored time scale, the temporal profile shows a slower growth taking place in the microsecond time scale. From the fitting of the signals to a first-order kinetics an estimation of the half-life of the formation of the transient species of about  $\sim 10 \mu\text{s}$  was obtained. Since these signals do not decay in our time scale, it can only be inferred that the lifetime of this transient species is longer than 5 ms. This is a longer lived transient species than that obtained from the previously reported PPV@CsX ( $\tau = 338 \mu\text{s}$ ), probably reflecting the influence of the methoxy substituents on the stability of the transient.<sup>1</sup>

The growth of this signal should be accompanied with the decay of another species in the same time scale ( $\sim 10 \mu\text{s}$ ). However, no spectroscopic evidence for this species being the precursor of our observed transient growth could be obtained. This may be due to the fact that the signals of the precursor are very weak and overlapped with the other more intense signals of the growing species. Triplet excited states are obvious candidates as the invisible precursor giving rise to a growth of the transient in the microsecond time scale.

With respect to the nature of the transient spectrum recorded by laser flash photolysis, most probably it does not correspond to dMeOPPV triplet excited state since this species is known to be completely quenched by O<sub>2</sub> and in our case no influence of the O<sub>2</sub> presence was observed. However, it may happen that the accessibility of the O<sub>2</sub> to dMeOPPV included in the intergallery space of montmorillonite is hindered as it has been observed in other cases.<sup>6</sup> Therefore, O<sub>2</sub> quenching is inconclusive to rule out triplet excited state as the transient responsible for the optical spectrum shown in Figure 5. This spectrum can be attributed to the dMeOPPV polaron based on the optical spectrum that is typical for a conducting polymer that generally extends over a broad wavelength range and that is different from the one reported for the triplet excited state of related dialkoxy PPV.<sup>25</sup> This assignment is compatible with a series of observations including the following: (i) the well-known ability of zeolites and clays to generate radical cations upon excitation of electron-rich aromatic molecules,<sup>6</sup> (ii) the insensitivity to the presence of O<sub>2</sub>, and (iii) the long lifetime of this transient species, since most encapsulated radical cations live longer than milliseconds and in some cases can even be detected by steady-state spectroscopic techniques. In addition, this assignment is in agreement with previous reports on the photochemistry of PPV encapsulated inside zeolites and with the intervention of these polarons on dMeOPPV electroluminescence.<sup>1</sup>

To get additional evidence in support of the photochemical generation of dMeOPPV polarons in the laser flash photolysis experiments, we did the same laser flash photolysis experiments purging the sample with MeOH vapors. MeOH is a well-known hole quencher<sup>21</sup> and therefore should be able to quench polarons. Figure 6 shows the transient signals monitored at 350 nm before and after purging the sample with MeOH vapor. As anticipated, the transient signal recorded after purging the sample with MeOH vapor is quenched, providing further support for the



**Figure 6.** Transient absorption signals monitored at 350 nm recorded for a dMeOPPV@montmorillonite sample before (a) and after (b) purging with MeOH vapor.

assignment of the transient species responsible for the spectra recorded under N<sub>2</sub> and O<sub>2</sub> atmosphere as the dMeOPPV polaron.

In summary, the introduction of two methoxy groups in the structure of the precursor of the PPV polymer requires of a branched monomer which is not able to diffuse through the faujasite micropores. However, it fits comfortably in the intergallery spaces of montmorillonite. The “in situ” polymerization, taking advantage of the basicity of the alkali-exchanged montmorillonite, gives a polymeric dMeOPPV@montmorillonite material which is photoluminescent and photostable even under oxygen atmosphere. The transient spectrum recorded by laser flash photolysis which is very long-lived corresponds to the dMeOPPV polaron. All these features make the new polymeric material very attractive for its application in PLEDs.

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