JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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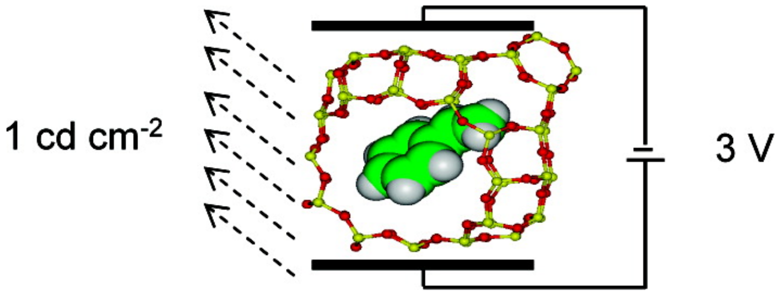
J. Am. Chem. Soc., **2007**, 129 (26), 8074-8075• DOI: 10.1021/ja0718265 • Publication Date (Web): 07 June 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Electrochemiluminescence of Zeolite-Encapsulated Poly(*p*-phenylenevinylene)

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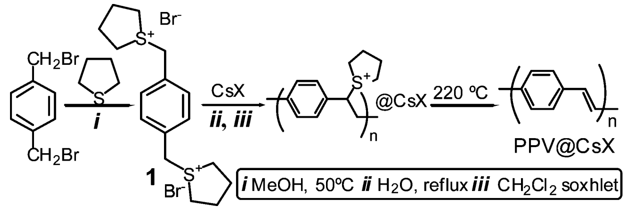
After the seminal work from Friend reporting the observation of electroluminescence from poly(*p*-phenylenevinylene) (PPV),[1] there has been a continuous interest trying to improve the performance and durability of organic light emitting devices (OLEDs) exploiting this PPV property. Two of the most important limitations of PPV are its poor stability in the presence of atmospheric oxygen leading to polymer degradation under operation conditions and the difficulty in the processability.

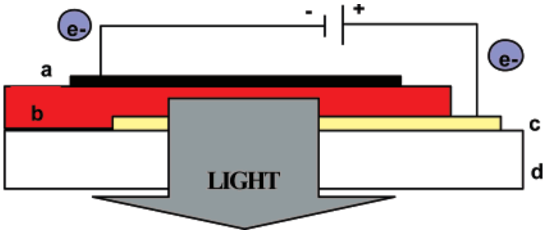
Zeolites have been widely used as hosts to incorporate organic molecules.[2−5] One of the most general consequences resulting from the incorporation of an organic guest inside the zeolite micropores is an enhancement of the stability and persistence of the organic molecules.[6] This increased stability is particularly remarkable in those cases in where a tight fit between the zeolite walls and the organic guest occurs. Stabilization arises frequently from the impeded attack of oxygen, water and other external reagents to the organic molecule. Also another general effect in many host−guest zeolite systems is an emission efficiency increase of the encapsulated guest owing to the fact that radiationless deactivation pathways are disfavored compared to emissive decay pathways as a consequence of guest immobilization.[6] Both effects, guest stabilization and enhanced emission, could be valuable for OLED development.

Among the organic guests that have been encapsulated inside zeolites, there are numerous reports describing the preparation of occluded conducting organic polymers, including polyacetylene, polyanilines, polypyrroles, and polythiophenes.[7,8] Recently, we have reported the preparation of PPV encapsulated in basic faujasites.[9] The key steps in the preparation of zeolite-encapsulated PPV are (i) the ion exchange introducing the bis-tetrahydrothiophenium monomer **1**, (ii) the thermal polymerization of **1** catalyzed by the basic sites of faujasites, and (iii) tetrahydrothiophenyl elimination leading to the formation of the vinylene units. Scheme 1 presents the route for the preparation of zeolite-encapsulated PPV.

Scheme 1. PPV Zeolite Encapsulation Preparation Process



Scheme 2. Parts of an Electroluminescent Cell Based on PPV@CsX: (a) Aluminum; (b) PPV@CsX; (c) ITO; (d) Glass



An application of zeolite-encapsulated PPV would be to develop OLED cells. This is a challenging task since no precedents about the construction of an OLED cell using zeolite matrices exist. In the present work we report the preparation of such a type of zeolite-based electrochemiluminescent cell as well as the influence on the electrochemiluminescence performance of the presence inside the zeolite particle of electron and/or hole injection dopants.

Two different materials starting from basic KX or CsX zeolites were prepared. Analytical and spectroscopic data of PPV encapsulated within KX or CsX zeolites (PPV@KX and PPV@CsX) showed that both solids contain around 3.5 wt % of well-formed PPV polymer. Of particular relevance is the solid-state ^{13}C NMR in where only sp^2 carbons appearing as a broad peak at 128 ppm were observed (Figure S1, Supporting Information), while the signals of the aliphatic carbons of tetrahydrothiophene moiety at 64 and 39 ppm were absent (Figure S2, Supporting Information). IR and optical spectroscopy are also in excellent agreement with the spectra for authentic PPV.[9] Also chemical analysis showed that the sulfur content of our PPV samples is below 0.1%. Electrochemiluminescent cells comprising a zeolite-encapsulated PPV as active layer were constructed using a transparent conductive indium tin oxide (ITO) anode and aluminum counter electrode. Scheme 2 shows the parts of the cells used to measure the electrochemiluminescent activity of the zeolite-encapsulated PPV.

These cells were submitted to a constant voltage of direct current (between 0−10 V) without observing any electroluminescence. In contrast to the electrolyteless zeolite-encapsulated PPV behavior, when the cell contains Praestol [a poly(acrylate-acrylamide) copolymer] as solid polyelectrolyte to promote charge migration then electrochemiluminescence from the cell was observed (Figure 1). The intensity of the emission depended on the voltage applied to the cell, the optimum voltage for maximum emission being 5 V. Both samples PPV@KX and PPV@CsX exhibited electrochemiluminescence, although the intensity of PPV@CsX was 1.5 times higher than that of PPV@KX. The latter observation could be due a combination of different factors but a possible explanation is the role of the alkali metal ion (either Cs$^+$ or K$^+$) influencing charge migration through the zeolite micropores. The electrochemiluminescent emission agrees with the photoluminescence of the zeolite-encapsulated PPV but lacking the fine structure characteristic of photoluminescence. Figure 1 shows a comparison between the electrochemiluminescent and photoluminescent emission.

In OLED cells it is known that the presence of electron or hole injection layers plays a crucial role in the efficiency of the cell.[10] In our case, the fact that PPV is encapsulated in the internal pores of the zeolite makes the presence of these layers inefficient. Thus, no influence on the electrochemiluminescence was observed when the aluminum cathode was covered by a thin film of poly-2,5-[3,4-(ethylenedioxy)thiophene] (PEDOT) as hole injection layer. This

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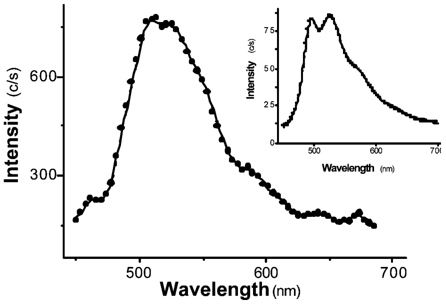
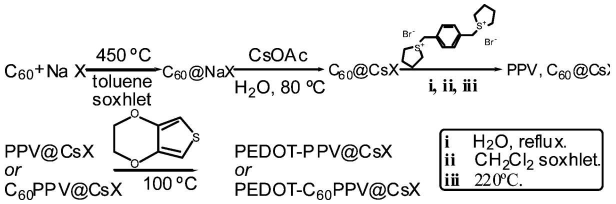


Figure 1. Emitted light intensity versus wavelength for a PPV@CsX electroluminescent cell operating at 5 V constant voltage. The inset shows the photoluminescence spectrum of PPV@CsX ($\lambda_{ex} = 370$ nm).

Scheme 3. Preparation of C_{60}– and PEDOT-doped PPV@CsX



fact may reflect the lack of interfacial contact between PEDOT and zeolite-encapsulated PPV.

To increase the zeolite-encapsulated OLED efficiency allowing for intimate contact between occluded PPV and the hole or electron injection dopants, we prepared three samples of PPV@CsX containing coadsorbed inside the zeolite pores either PEDOT, as hole injection dopant,[10] or C_{60} as electron injection dopant,[11] or both simultaneously. Coadsorption of C_{60} was simply achieved by thermal treatment of a mechanical mixture of C_{60} and NaX at temperatures above 450 °C. The sample was later Cs^+ exchanged before synthesizing PPV by the usual procedure. Those samples contain about 1 C_{60} every 10 supercages. The internal location of C_{60} inside the pores has been demonstrated previously.[12] Scheme 3 shows the actual preparation procedure of (PPV/C_{60})@CsX.

On the other hand, preparation of PEDOT incorporated inside zeolites has been recently described by adsorbing 3,4-ethylenedioxythiophene on iron-doped zeolite.[13] Formation of the corresponding encapsulated PEDOT polymer was evidenced visually by the development of green color. In the same way, starting from PPV@CsX and after impregnation with $FeCl_3$, PEDOT polymer was formed inside the zeolite rendering (PEDOT/PPV)@CsX. Finally, a sample containing simultaneously PPV as light emitting component and C_{60} and PEDOT as dopants was prepared by first incorporating C_{60} at 450 °C, then forming PPV at 250 °C and finally forming PEDOT at 100 °C. Scheme 3 describes the preparation of these samples PEDOT-C_{60}PPV@CsX.

Electrochemiluminescence measurements of the series of samples containing zeolite-encapsulated PPV and the presence of one or two dopants clearly reveal that, in contrast to the lack of influence of a PEDOT layer deposited on the electrodes on PPV@CsX, coadsorbed dopants can play the expected role when they are also incorporated inside the zeolite pores (see Figure 2).

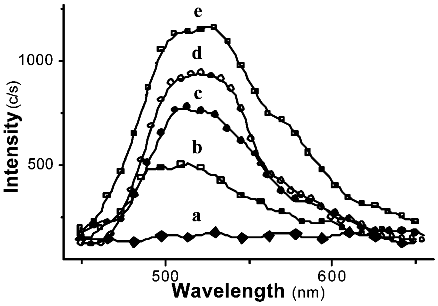


Figure 2. Emitted light intensity versus wavelength for (a) PPV@CsX at 0 V, (b) PPV@CsX at 5 V, (c) (PPV, C60)@CsX at 5 V, (d) (PPV, PEDOT)@CsX at 5 V, (e) (PPV, PEDOT, C60)@CsX at 5 V.

In this way, the electrochemiluminescence efficiency increased upon co-incorporation of C_{60} or PEDOT. The sample containing simultaneously the three components (PEDOT/PPV/C_{60}@CsX) gave the best results with an overall efficiency as compared to plain PPV@CsX of 6-fold increase. The estimated luminance of the (PPV, PEDOT, C_{60})@CsX cell using a calibrated radiometer was about 1 cd × m^2.

In conclusion, we have developed an electrochemiluminescent cell based on zeolite-encapsulated PPV that operates at about 5 V of constant voltage using Praestol as solid electrolyte. The electroluminescence efficiency depends on the charge balancing cation, being higher for Cs^+ than for K^+. Doping by co-adsorption of electron and hole injection dopant increases the efficiency of the cell. Given the advantages in processability and stability of zeolite powders, it can be anticipated new research for other related zeolite-based electroluminescent cells.

Supporting Information Available: Solid-state MAS ^{13}C NMR spectra of the polymeric precursor and PPV@CsX. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0718265