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Highly Photoconducting π-Stacked Polymer Accommodated in Coordination Nanochannels

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Ⓢ *Supporting Information*

ABSTRACT: We report on the formation of single poly(*N*-vinylcarbazole) (PVCz) chains in one-dimensional channels of $[\mathrm{La}(1,3,5\text{-benzenetrisbenzoate})]_n$, where the side carbazolyl groups of the confined PVCz are effectively π-stacked. This ideal conformation of PVCz chains in the coordination nanochannels contributed to a drastic increase in hole mobility, which was 5 orders of magnitude higher than that in the bulk state. It is also noteworthy that PVCz isolated from the nanchannels still had a high hole mobility.

Conductive polymers with charge-transporting properties play important roles in electronics technology and advanced functional materials.[1] In these materials, it is widely recognized that the conformations of the polymer chains, and related properties such as the persistence length, molecular order, and packing structure, have considerable effects on the conducting properties. In general, organic polymeric conductors do not show relatively high conductivities because their low structural regularity and random chain entanglement result in disruption of the continuous conducting pathway. Thus, spatial control of polymer chains to enhance the conformational order and molecular packing is a great challenge for achieving organic polymers with higher conductivities.[2−5]

As a typical class of hole-transporting polymers, poly(*N*-vinylcarbazole) (PVCz) and related side-chain polymers with pendant carbazolyl groups have attracted much attention because of their photoconductive properties and their ability to form stable radical cations (holes).[6−12] PVCz is the first and most widely studied organic polymeric photoconductor. PVCz and its related polymers find their applications in electrophotography, light-emitting diodes, photorefractive materials, and photovoltaic devices.[13−16] In the process of photoconductivity of PVCz, charge carriers are generated at the side chain under photoirradiation, and this is followed by hopping of the holes to neighboring carbazole moieties. This hole transport is largely attributed to the $\pi-\pi$ stacking arrangement of the carbazolyl groups. However, in conventional bulk PVCz, a partial π-stacked conformation with isolated monomeric sequences has been proposed because of the low stereoregularity of the side chains.[10,11,17] Thus, the carriers do not move with uniform velocity, and they reside mostly at localized (trap) sites because of the disordered amorphous form. This trapping process is responsible for the low hole mobility in bulk PVCz (10^{-7} cm^2 V^{-1} s^{-1}).[9,10] This is supported by the fact that the disorder formalism has been successfully applied to the analysis of charge-carrier transport in the bulk materials observed in time-of-flight measurements with long-range translational motion, giving almost perfect interpretations of the transport mechanism.[18,19] In this regard, it has been predicted that alignment of the carbazole groups with a face-to-face conformation would considerably improve the hole mobility in PVCz, which would lead to a drastic conceptual shift of PVCz from the conventional disordered system to an ideal ordered one.[10,11,20] However, to date, this idea has not been realized because of the difficulty of controlling the arrangement of the PVCz chains.

Our strategy for increasing the hole mobility in PVCz involves incarceration of the polymer chains into regular microporous channels. In fact, polymer inclusion in regular microporous hosts, such as crystalline organic hosts, has attracted much attention because this approach can provide extended chains in restricted spaces.[21−26] However, the narrow (4−6 Å) and fragile channel structure of these hosts formed by hydrogen bonding or weak van der Waals interactions cannot allow the incorporation of polymer chains with bulky side chains. Recently, porous coordination polymers (PCPs) composed of metal ions and bridging organic ligands have been extensively developed because of their diverse structures with pore sizes and shapes that are controllable at the molecular level.[27−33] Taking advantage of the pore characteristics of PCPs can provide key opportunities for controlling the conformation and alignment of confined polymers.[34−37] For our purpose, utilization of one-dimensional PCP channels whose pore size approximates the thickness of PVCz chains would enhance the $\pi-\pi$ stacking of the carbazole moieties. Here we employed as a PCP matrix $[\mathrm{La}(1,3,5\text{-benzenetrisbenzoate})]_n$ (**1**), in which the size of the one-dimensional channels is 10.7 Å.[38] Polymerization of vinyl carbazole (VCz) adsorbed in the channels of **1** provided a PCP−PVCz nanocomposite.[34,35] On the basis of the molecular dimensions of VCz (8.7 Å × 7.5 Å), the

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nanochannels can accommodate only single chains of PVCz with a linear conformation, which enhances the $\pi-\pi$ stacking of the carbazoles. Thanks to this unusual conformation, the hole mobility of PVCz in **1** increased by ca. 10^5 times compared with that of bulk PVCz. Moreover, the chain orientation of PVCz was not severely disturbed during the process of isolating the chains from the PCP matrix, and the recovered PVCz still showed a much higher hole mobility than bulk PVCz.

To accommodate PVCz in microporous channels, radical polymerization of VCz was performed in the framework of **1** at 70 °C for 48 h.[34,35] The obtained product was washed with acetone and methanol to remove unreacted monomer, affording the PCP−PVCz composite (**1**⊃PVCz). The conversion from VCz to PVCz was calculated to be ca. 80%, and the loading amount of PVCz accommodated in **1** was 0.44 (weight of PVCz/weight of **1**), which was consistent with the results of thermogravimetric analysis (TGA). In the IR spectrum of **1**⊃PVCz, the peak for the C═C stretch of VCz at 1638 cm^{-1} was almost undetectable. Powder X-ray diffraction (PXRD) measurements of **1**⊃PVCz indicated that the channel structure of **1** was maintained during the polymerization (Figure 1a). Scanning electron microscopy (SEM) showed that the morphology (size, shape, and surface) of the rod-shaped particles of **1** remained unchanged during the polymerization (Figure 1b, c). This suggested that the polymerization of VCz proceeded inside the channels of **1**. Furthermore, a dramatic decrease in the nitrogen adsorption capacity of **1**⊃PVCz at 77 K compared with that of **1** alone is consistent with the encapsulation of PVCz chains in the channels. The configuration of the PVCz chains confined in the channels of **1** was studied using molecular dynamics (MD) method (Figure 2). In this MD simulation, the conformational structure of the confined PVCz was very different from that of bulk PVCz and represented a single-chain conformation with a linearly extended structure. It seems that the carbazole groups in the side chain were stacked to have intimate interactions in the narrow channels.

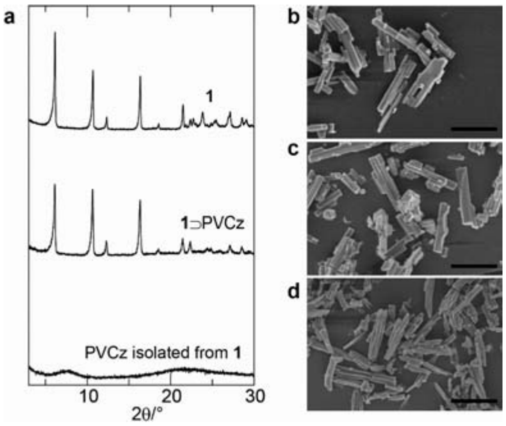

Figure 1. (a) PXRD patterns of **1**, **1**⊃PVCz, and PVCz isolated from **1**. (b−d) SEM images of (b) **1**, (c) **1**⊃PVCz, and (d) PVCz isolated from **1**. Scale bars correspond to 10 μm.

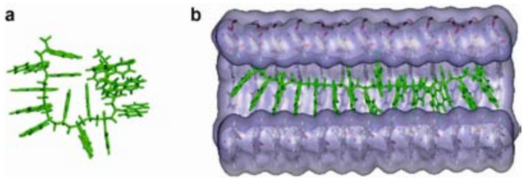

Figure 2. MD structures of a PVCz 15-mer (a) in the bulk state and (b) accommodated in a channel of **1**. The stereoregularity of the model oligomer was similar to that of the real PVCz.

Fluorescence measurements are useful for determining the stacking structure of the carbazole side groups in PVCz, in which fully and partially overlapped structures of neighboring carbazolyl chromophores give singlet excimers with fluorescence maxima at 420 and 370 nm, respectively.[39,40] As shown in Figure 3a, no emission was observed from the host PCP **1** alone. The fluorescence spectrum of PVCz in a dilute tetrahydrofuran (THF) solution showed a main peak for excimer emission of the partially overlapped carbazole groups at ca. 370 nm, because of the syndiotactic-rich structure of PVCz.[17,39,40] In contrast, bulk PVCz gave a fluorescence spectrum with a strong peak for the full-overlap excimer at 420 nm together with a weak shoulder at 370 nm (Figure 3a).[39,40] This increment of full-overlap excimer results from molecular packing in the solid bulk state. We then checked the spectrum of **1**⊃PVCz and found that fluorescence from the full-overlap excimer became major and the shoulder peak ca. 370 nm could not be appreciably detected, suggesting the formation of π-stacked carbazoles with a enhanced fully overlapped conformation (Figure 3a). Also, the emission peak of **1**⊃PVCz was slightly red-shifted relative to that of bulk PVCz, probably because close packing of the carbazole groups enhanced the electronic interactions, reducing the delocalized excited energy level.[4] Interestingly, the excitation spectrum of **1**⊃PVCz was dissimilar to the broad spectrum obtained from bulk entangled PVCz but analogous to that of PVCz in dilute solution (Figure 3b). This result reveals that there were no interchain interactions among PVCz chains in the channels of **1** during the excitation process.[41,42] Thus, on the basis of these fluorescence and excitation spectra measurements, it is likely that the intrachain fully overlapped structure of carbazole groups is dominant in **1**⊃PVCz.

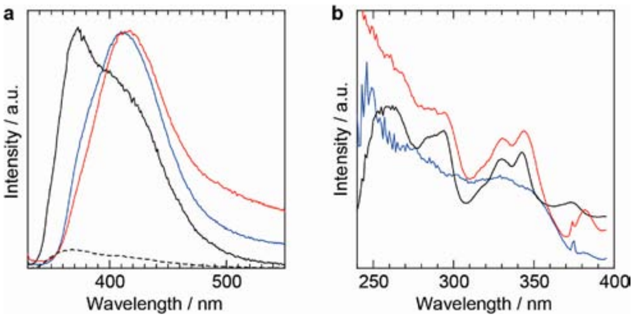

Figure 3. (a) Fluorescence spectra (excitation at 300 nm) of **1** (dashed), PVCz in a 5.4×10^{-5} M THF solution (black), bulk PVCz (blue), and **1**⊃PVCz (red). (b) Excitation spectra (fluorescence at 410 nm) of PVCz in THF solution (black), bulk PVCz (blue), and **1**⊃PVCz (red).

The overall characterizations of **1**⊃PVCz indicate the accommodation of single PVCz chains in the channels with a conformation having mostly a face-to-face orientation of the carbazolyl groups, which should lead to an improvement of the hole mobility in PVCz. To verify this hypothesis, we studied the transient photoconductivity ($\phi\sum\mu$) of **1**⊃PVCz using flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements, in which ϕ and $\sum\mu$ are the charge-carrier

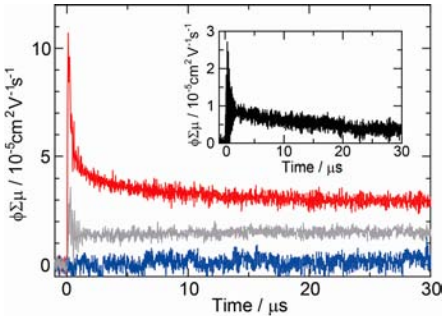

Figure 4. Transient conductivities observed for **1** (gray), bulk PVCz (blue), **1**⊃PVCz (red), and PVCz isolated from **1** (inset). The transients were recorded under 355 nm laser pulse excitation at 4.6 × 10^{15} photons cm^{-2}.

generation yield and the sum of the charge-carrier mobilities, respectively.[43−45] As shown in Figure 4, bulk PVCz did not give any transient photoconductivity signals. This is the case because the disorder of the molecular alignment in the bulk amorphous state gives structural defects that act as trapping sites for positive charge carriers.[10,11] As a result, conventional time-of-flight measurements showed that the hole mobility (μ) for bulk PVCz is low (10^{-7} cm^2 V^{-1} s^{-1}).[9,10] In contrast, **1**⊃PVCz displayed a clear conductivity signal, where the maximum transient conductivity rapidly reached values as high as 1×10^{-4} cm^2 V^{-1} s^{-1} (Figure 4). No dependence of the transient conductivity on the excitation density of laser pulses was seen in this system. In addition, the transient conductivity profile for the host **1** alone did not show such a rapid increase (Figure 4). Introduction of *N*-methylcarbazole into the channels of **1** did not affect the conductivity, indicating no electronic interaction between the host framework and the guest carbazole molecules. Bulk mixing of **1** with PVCz did not improve the transient conductivity. Thus, the high conductivity observed in **1**⊃PVCz resulted from the single PVCz chains accommodated in **1**. The value of μ in **1**⊃PVCz was calculated to be 2×10^{-2} cm^2 V^{-1} s^{-1} on the basis of the values of $\phi\sum\mu$ and ϕ derived from TRMC and transient absorption measurements, respectively. This hole mobility is extremely high, exceeding that found in conventional bulk PVCz by 5 orders of magnitude. This is ascribable to the enhanced π-stacking in the carbazole arrangement of the confined PVCz.[10−12,20] Despite the π-stacked nature, the hole-transporting ability of PVCz in **1** is as high as that of high-performance π-conjugated polymers, such as poly(phenylenevinylene)s (10^{-2} to 10^{-1} cm^2 V^{-1} s^{-1}) and regioregular polythiophenes (10^{-2} to 5×10^{-1} cm^2 V^{-1} s^{-1}), as determined by TRMC measurements.[43−45] It has been predicted that an ultimate PVCz without any trapping sites and structural disorder would show a hole mobility of 3×10^{-1} cm^2 V^{-1} s^{-1}.[11,20] Thus, the arrangement of PVCz in the channels of **1** should be close to the ideal conformation of PVCz for attaining high conductivity.

PVCz accommodated in **1** could not be recovered by solvent extraction because of the strong confinement in **1**.[46] Thus, isolation of PVCz from **1**⊃PVCz was performed by dissolving the host framework in aqueous sodium ethylenediaminetetraacetate (Na EDTA) solution, which gave PVCz as a white precipitate. Characterization of the resulting powder by PXRD (Figure 1a), TGA, gel-permeation chromatography, and NMR measurements showed the typical characteristics of syndiotactic-rich PVCz without any impurities (M_n = 21 000, M_w/M_n = 1.9; polystyrene standards). In SEM measurements, it is of considerable interest that the morphology of the recovered PVCz objects retained the microrod shape of the original host and composite particles, showing that the orientation of polymer chains was macroscopically maintained (Figure 1d). An electron diffraction pattern of the host microrod crystals revealed that the direction of crystal growth is parallel to the *c* axis. Since the channels of **1** penetrate along the *c* axis, the polymer chains are aligned along the long axis of the PVCz microrods. We measured the TRMC for the isolated PVCz and found that the hole mobility was 1×10^{-3} cm^2 V^{-1} s^{-1} (Figure 4). Although the chemical composition and structure of the isolated PVCz were exactly same as those of pure PVCz, this value is much higher than that obtained from PVCz in the bulk state, probably because the orientation of the PVCz chains was not severely disturbed during the isolation process. Notably, this PVCz sample did not exhibit a TRMC signal after dissolution in toluene and subsequent reprecipitation, indicating the importance of the chain arrangement in PVCz as a hole-transporting material.

In conclusion, we have demonstrated a simple methodology for the preparation of well-organized PVCz with extremely high hole mobilities by using a microporous PCP as a host. These results illustrate that spatial control of the polymer chain arrangement is a key strategy for attaining higher conductivities of organic polymers. In this regard, numerous other types of functional polymers with electronic or optical properties, such as π-conjugated polymers, can be introduced into the pores of PCPs in efforts to improve their properties. We believe that our system will thus contribute to the preparation of a variety of advanced nanocomposite materials based on PCPs and functional polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, TRMC measurements, crystal structure, TGA curves, adsorption isotherms, IR and NMR spectra, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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