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Intercalative Polymerization

Fabrication of Two-Dimensional Polymer Arrays: Template Synthesis of Polypyrrole between Redox-Active Coordination Nanoslits**

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In recent years, remarkable progress has been made in the area of coordination polymers with open structures, largely because of their diverse topologies and applications in storage,[1] separation,[2] and guest alignment.[1b] Control of molecular conversion or catalysis within the nanospaces of these coordination polymers is an important topic in this area.[3] In particular, open coordination frameworks with redox activity might be capable of controlling reactions and orienting oxidized or reduced products within the resulting crystalline composites. However, only a few cases that use coordination frameworks in the field of redox reactions have been reported.[4,5] This is because, in many cases, the host frameworks decompose during the redox reactions.[5]

The construction of well-defined polymer architectures is one of the most important issues in contemporary polymer and materials science.[6] Structures with two-dimensional organization are of particular interest because of their potential for offering optimized optical or electrical functions.[7] Intercalative polymerization within crystalline-layered host materials is a useful method to restrict the resulting polymers within the regular 2D spaces.[8] If the host matrices could be removed without disturbing the polymer assembly, then layered polymer objects, with morphologies directed by the host structure, would be obtained. Such a methodology will allow us to create novel polymer materials with structural order on the molecular level and with highly controlled morphologies and properties.[9]

Herein, we report an intercalative polymerization of pyrrole (Py) by oxidative polymerization within a layered framework of a redox-active coordination polymer, $[\{Ni(dmen)_2\}_2\{Fe^{III}(CN)_6\}]PhBSO_3$ (**1**; dmen = 1,1-dimethylethylenediamine; $PhBSO_3^- = p$-phenylbenzenesulfonate).[10] In the oxidation process, the $[Fe^{III}(CN)_6]^{3-}$ units act as a stable redox-active modules, because the reduced $[Fe^{II}(CN)_6]^{4-}$ units can retain a similar coordination geometry. We also examined the subsequent removal of the host layers from the resultant nanocomposite for controlling the morphogenesis of polypyrrole (PPy).

Oxidative polymerization of Py within the nanoslits of **1** was performed by reaction of the host complex **1** with neat Py at 333 K for 48 h in the presence of a small volume of water to induce the polymerization.[11] During the polymerization reaction, the color of the sample changed from light brown to dark green, which suggested the production of π-conjugated PPy (Figure 1a). The solid-state UV/Vis reflection spectrum of the resultant composite **2** showed additional absorption bands around 360 and 900 nm, which could be attributed to PPy (Figure 1a).[12] Scanning electron microscopy (SEM) images of **1** and **2** indicated that the morphology and size of the crystals were retained during the polymerization, and the adhesion of polymeric substances on the surface of **2** was not observed (see the Supporting Information).

To examine the polymerization mechanism, we conducted IR, magnetic, and energy-dispersive X-ray (EDX) measurements of **1** and the composite **2**. The IR spectrum of **1** showed a sharp band for ν(CN) of the $[Fe^{III}(CN)_6]^{3-}$ unit at 2122 cm^{-1} (see the Supporting Information). In contrast, ν(CN) in **2** shifted to a lower wavenumber, around 2060 cm^{-1}, which was assigned to the $[Fe^{II}(CN)_6]^{4-}$ unit.[11] In addition, the IR spectrum of the composite showed the absence of the bands attributed to the counterions ($PhBSO_3^-$) of the host framework. The disappearance of $PhBSO_3^-$ was also supported by EDX microanalysis of **1** and **2**, which showed a decrease in atomic content of sulfur from 1.56% to 0.19% (see the Supporting Information). The temperature dependence of the magnetic susceptibility during the polymerization is shown in Figure 1b. The host **1** showed typical ferromagnetic behavior, with a critical temperature (T_c) of 9.5 K.[10] After reaction with Py for 12 h, the magnetization values of the product decreased and a lower T_c value of 5.5 K was observed. No transition was observed in the final product obtained after polymerization for 48 h. These gradual changes indicated that the paramagnetic Fe^{III} ions were reduced to diamagnetic Fe^{II}

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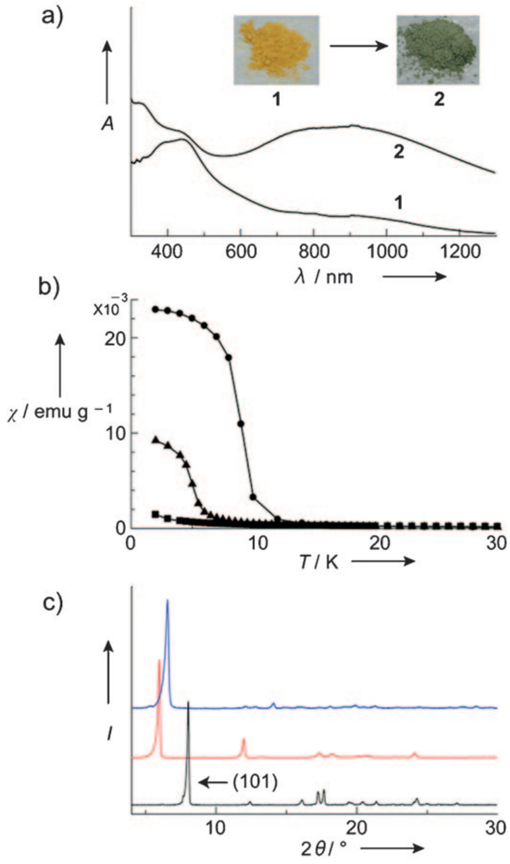


Figure 1. a) UV/Vis reflection spectra for **1** and **2**. b) Temperature dependences of magnetic susceptibility measured under an applied dc field of 500 Oe for **1** (circle), the polymer composite obtained after polymerization for 12 h (triangle) and 48 h (square). c) XRPD patterns for **1** (black), the solid obtained after soaking **1** in Py (red), and **2** (blue).

ions and the magnetic domain fragmented during the polymerization.[12] Thus, in this system, the $PhBSO_3^-$ ions were liberated for charge compensation during the polymerization process.

The polymerization mechanism outlined above was also supported by X-ray powder diffraction (XRPD) measurements. The host **1** comprises two-dimensional layers with a thickness of 9.8 Å on the (101) plane; the long anions ($PhBSO_3^-$) act as pillars and separate the layers with an interlayer separation distance of 11.0 Å (see the Supporting Information). In our previous work on a series of the bimetallic 2D assemblies $[\{Ni(dmen)_2\}_2\{Fe(CN)_6\}]X$ (X = counteranion), the interlayer distances were found to be elongated or shortened by the adsorption or desorption of guest molecules.[10] Similarly, the XRPD patterns show the expansion of the interlayer distance of **1** after soaking in Py (interlayer distance = 14.8 Å, Figure 1 c). This result confirms the intercalation of Py between the host layers. Interestingly, the XRPD pattern of the nanocomposite **2** (interlayer distance = 13.5 Å) shows a sharp diffraction peak, which is different from those of **1** and the **1**-Py adduct. The observed increase in the interlayer separation upon formation of **2** from **1** suggests that a monolayer of PPy was arranged between the host layers. Similar arrangements have been observed in the cases of the nanocomposites of inorganic layered hosts with PPy.[8a,c,e] The reduction of the interlayer separation from the **1**-Py adduct to **2** could be attributed to the release of the pillar anions ($PhBSO_3^-$), which is in good agreement with the IR and EDX results.

From these results, the overall polymerization can be described by the intercalative and oxidative polymerization within the 2D coordination nanospace (Figure 2). In this reaction, Py monomers are intercalated into the nanoslits and are oxidized by the Fe^{III} ions in the host layers. As a consequence of the host–guest redox reaction, the Py monomers are converted into PPy, and the Fe^{III} ions are reduced to Fe^{II} ions, accompanied by the release of the pillar counterions for charge compensation.

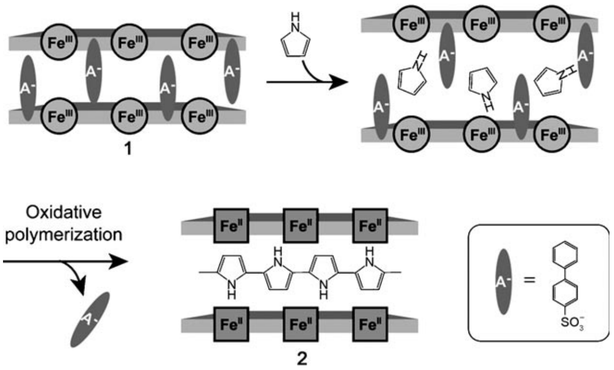


Figure 2. Schematic illustration of the intercalation of the Py monomer and the oxidative polymerization of Py by the Fe^{III} ions in the host layers.

To elucidate the importance of the redox-active Fe^{III} sites in the host framework, we prepared a redox-inert complex $[\{Ni(dmen)_2\}_2\{Co^{III}(CN)_6\}]ClO_4$ (**3**)[10] as a structural analogue of **1**. Although we carried out the polymerization of Py in **3** under the same conditions as in **1**, no polymerization reaction occurred (see the Supporting Information). This indicated that the electron transfer between the host matrix and the guest monomers or polymers is a key factor in this unique in situ polymerization.

Template synthesis has the potential to control the structure and morphology of the products obtained after removal of the host matrices.[9,13] Removal of the host framework of **2** in a solution of ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, 0.05 N) allowed the isolation of the intercalated PPy as an insoluble black precipitate. The PPy was successfully characterized by XRPD, SEM-EDX, IR, and UV/Vis absorption measurements (see the Supporting Information).[14] The controlled morphogenesis of the isolated polymer objects was evident from the SEM images. A granular morphology[15] was observed for a bulk PPy prepared by oxidation of Py with $K_3[Fe^{III}(CN)_6]$ in water.[14b,16] In contrast, the morphology of the PPy isolated from **2** is finely plated (Figure 3). At high magnification, the SEM image of the isolated PPy showed a discernible stack of thin layers. A molding effect is evident from the morphological transcription from the layered coordination matrix in **2** to the polymer

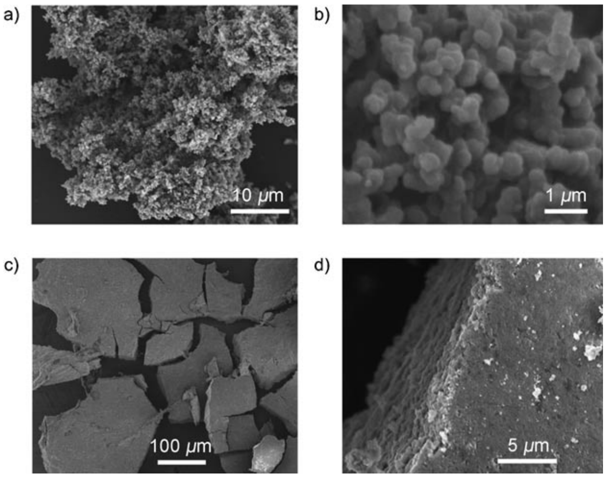


Figure 3. a) and b) SEM images of the bulk PPy. c) and d) SEM images of the PPy isolated from **2**.

texture: polymer chains are prepared within the two-dimensional nanospace and are then isolated from the composite while retaining their orientation, which results in sheet-stacking polymer architectures.

To investigate the detailed microstructure of the PPy isolated from **2**, we carried out XRPD, small angle X-ray scattering (SAXS), and electrical conductivity measurements. Figure 4a shows the XRPD patterns of the PPy isolated from **2** and the bulk PPy. In this analysis, the bulk PPy was found to be an amorphous compound. The XRPD profile of the PPy isolated from **2** showed a few peaks, including the peak at $2\theta = 22.8°$ ($d = 3.9$ Å), which may correspond to the interplanar distance for Py rings; this indicates the accumulation of aromatic planes of PPy.[17] Furthermore, the XRPD pattern of the PPy isolated from **2** showed a considerable increase in intensity below $2\theta = 10°$. To investigate the higher-ordered structure, we performed a SAXS measurement on the PPy isolated from **2**. The SAXS profile exhibited a shoulder peak, which is attributable to the existence of a nanodomain structure of PPy (the domain size was about 1–4 nm, Figure 4b).[18] These results suggest that the platy nanodomains, composed of accumulated PPy, may aggregate and stack to form microplate objects (Scheme 1). Direct information on the molecular orientation in the PPy isolated from **2** was obtained by electrical conductivity measurements of a single PPy microplate. The conductivities parallel to the plate ($\sigma_{\parallel}$) and perpendicular to the plate ($\sigma_{\perp}$) were successfully measured by the two-probe method (Scheme 1, see the Supporting Information). The as-prepared PPy microplate showed very low conductivity along both directions ($<10^{-8}\,\mathrm{S\,cm^{-1}}$). However, after doping with iodine vapor, the conductivities of the PPy microplate increased;[19] the conductivity along the direction parallel to the plate ($\sigma_{\parallel}$) was $4.6 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$, which was higher than that along the direction perpendicular to the plate ($\sigma_{\perp} = 2.3 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$). This anisotropic conduction ($\sigma_{\parallel}/\sigma_{\perp} = 20$) clearly indicated that the PPy chains are oriented preferentially along the direction parallel to the sheets.[20] Therefore, in this system, the crystalline template **1** successfully directed the structural order and orientation of PPy assembly on the molecular level. Much work has been devoted to intercalative polymerizations in inorganic layered hosts,[8] but control of the structural order and molecular orientation by isolation of polymers from layered nanohybrids is still unexplored. In addition, this is the first example of the transcription of morphology and orientation from host coordination frameworks to objects formed within the framework and subsequently isolated.

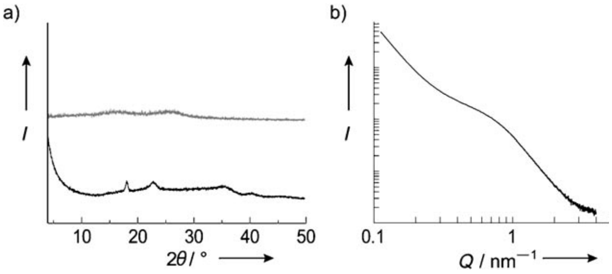
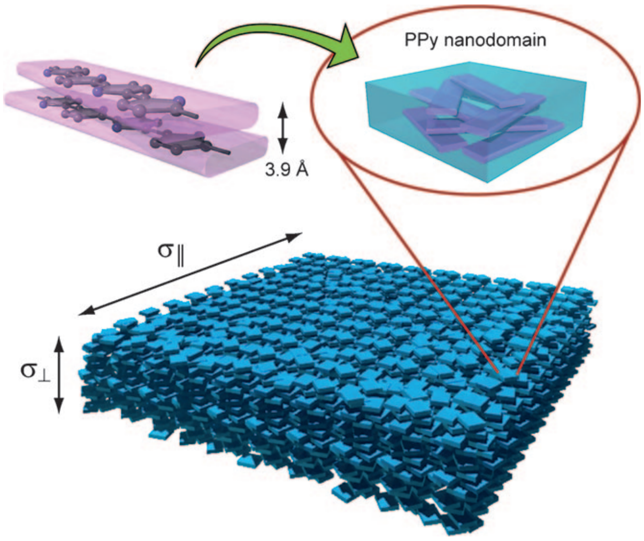


Figure 4. a) XRPD patterns of PPy isolated from **2** (black) and bulk PPy (gray). b) SAXS profile for the PPy isolated from **2**.



Scheme 1. Schematic representation of how the PPy nanodomains composed of accumulated plane polymers might organize themselves to form the plate architecture. The directions of the conductivities parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the plate are also shown.

In conclusion, we have successfully carried out the intercalative and oxidative polymerization of Py within a redox-active layered coordination polymer with maintenance of its crystallinity and morphology. We have also achieved the fabrication of oriented polymer microplates, which result from the two-dimensional confinement of the polymer chains within the nanocomposite. This methodology will contribute to the development of coordination polymers with open structures for their application as attractive reaction containers and templates, because the strategy of synthesizing compounds transcribed from coordination-polymer crystals provides access to further forms of several different types of materials, for example, carbon, metals, and metal oxides, with a range of shape-tunable properties.

Experimental Section

Polymerization of Py between the host layers: The host **1** (800 mg) was prepared by drying under vacuum at 423 K for 3 h. Dry **1** was then immersed in pyrrole (4 mL) and water (1 mL) at room temperature under N_2 in a pyrex reaction tube. The reaction tube was heated at 333 K for 48 h. The resultant powder was filtered and washed repeatedly with chloroform to yield the composite material **2**.

Isolation of PPy from **2**: The composite **2** (800 mg) was stirred in a 0.05 N aqueous solution of Na_2EDTA for 12 h to completely decompose the host framework. The black precipitate was collected and washed several times with water. Subsequent drying under vacuum at room temperature yielded PPy (17 mg).

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