

# Sub-nano Scale Molecular Self-assembly for Nanotechnology Applications

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**Abstract:** The design of molecular order at economically viable method is a challenging for materials science research. Here we report the one step process in induced molecular ordered in polypyrrole through cross-linking with ZnCl<sub>2</sub>. Resulting nanostructure show hexagonal diffraction pattern in metal organic frame work by transmission electron microscope with high conductivity in comparison to uncross-linked polypyrrole.

**Keywords:** Polypyrrole, Molecular ordering, HRTEM, Semiconductor, Cross-linking

## I. INTRODUCTION

In an area of nanotechnology, three-dimensional (3D) molecular ordering is an important and challenging aspect in an of materials science [1-3]. The 3D ordering can improve the efficiency of devices. Self-assembly is an emerging and powerful approach to fabricating nanostructured materials. However, it faces challenge in controlling the arrangement of molecules at molecular level [4,5].

In materials science research, conducting polymers have received attention due to its facile synthesis approach, lightweight and flexibility [6]. Therefore, frequent efforts have been made to use conducting polymers for various electronic devices, such as organic photovoltaics [7], organic light-emitting diodes [9], and organic field-effect transistors [8]. However, its shows limitation due to chain entanglements and presence of amorphous regions in film which act as an impurity. Thus, broad research is needed to increase the long range order in conducting polymers system to improve the performance of conducting polymer based electronic devices. Several research groups have attempted to develop chemical and physical methods to improve the crystallite. Researcher tried to modified polymer backbones or side chains to improve the interactions among the polymer chains either through hydrogen bonding or  $\pi$ - $\pi$  stacking [6]. However, in the study of crystalline conducting polymers, the difficulty is in controlling the precise arrangement of polymers through economically viable process. Cross-linked polymers are widely used in various devices due to their high mechanical strength or solvent resistance during device fabrication. Unlike typical research on cross-linked polymers, our group has used controlled crosslinking techniques for precisely ordering in polymers. We reported molecular ordering in poly(2-vinylpyridine)(P2VP)[10] through self-recognition and organization during the chemical reaction of poly(2-vinylpyridine)/ polyaniline with cross-linker [11].

Since the crosslinking of molecules under controlled conditions, suppress the directional freedom of polymers and decreased chain entanglements. Therefore, molecular ordering by crosslinking may be a solution to resolve the inherent morphological limitations of the conducting polymers. For this study, we had cross-linked polypyrrole with Zn ions to induce

molecular-scale ordering in cross-linked polypyrrole using a simple solution process.

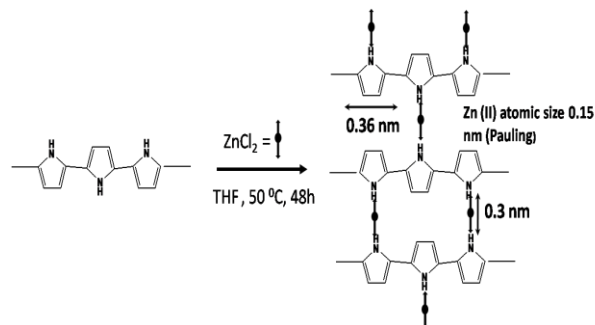


Fig.1. Scheme for molecular ordering in Polypyrrole and reaction condition.

## II. EXPERIMENTAL SECTION STARTING REAGENTS

Polypyrrole (PPy) (5 wt% solution in water), and zinc chloride (ZnCl<sub>2</sub>) and tetrahydrofuran were purchased from Sigma Aldrich. All materials were used as received without further purification. Glass substrates were purchased from Marienfeld-Superior.

Cross-linking of PPy with Zn<sup>2+</sup> ions was carried out in tetrahydrofuran (THF) for 48 h at 50 °C temperature (pyrrole repeating/ Zn ions mole ratio 1/0.8) and resulting sample were characterized by XRD, transmission electron microscope and conductivity of film was measured by four probe method after dialysis through membrane (cutoff MW =3000). Thin film XRD spectra was obtain using Reguka XRD instrument. Glass substrates were cut to a size of 15 × 15 mm<sup>2</sup>. Then, the cut glass pieces were ultra-sonicated with deionized water, acetone (Sigma-Aldrich) and isopropyl alcohol (Aldrich) for 15 min each. The washed glass pieces were dried in an oven at 60 °C, and their surfaces were exposed by means of UV-ozone to produce hydrophilic groups. The solution mixtures of PPy-Zn ions spin-coated or drop-cast on the glass substrates and coated films were then annealed at 150 °C for hours.

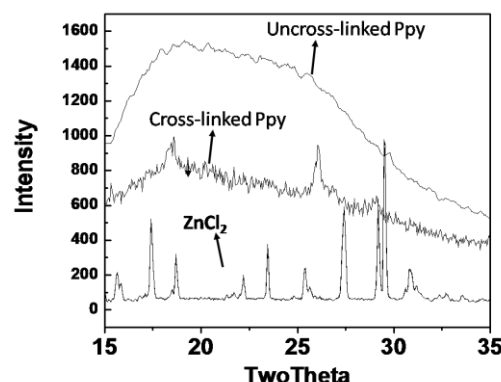


Fig. 2. Thin film XRD spectra of ZnCl<sub>2</sub>, uncross-linked polypyrrole (Ppy) and cross-linked Ppy with ZnCl<sub>2</sub>.

For XRD spectra, films were prepared by drop casting the solution (150  $\mu$ l) onto glass substrates (15  $\times$  15 mm<sup>2</sup>), and XRD measurements were performed on a Rigaku D/max-2500 diffractometer with Cu-K $\alpha$  radiation ( $\lambda$  = 1.54  $\text{\AA}$ ) at 40 kV and 100 mA. A high-resolution electron microscope (JEOL Ltd, 200kV). The specimens were prepared by drop-casting the Ppy-Zn ion cross-linked solution (15  $\mu$ l) on carbon-coated copper grids (200 mesh, EM Science) and annealed at 150  $^{\circ}$ C for 12 hours. The sheet resistances of Ppy-Zn cross-linked, Ppy control solution films ( $\sim$ 100 nm) were measured using a 4-point probe method from FPP-RS8 (Dasol Eng.). The mean value of the electrical conductivity of each film was calculated from the sheet resistances of 6 samples measured at room temperature. The film thickness of each film was measured using a surface profiler (NanoMap-LS).

### III. RESULTS AND DISCUSSION

Metal-organic interactions generate hybrid metal-organic frameworks (MOFs). For the growth of metal-organic coordinated structures, in liquid state we select low molecular weight Ppy and used pyrrole repeating unit: Zn ion mole ratio at 1.25. Model for generation of molecular order in cross-linked Ppy shown in Fig.1. The XRD spectra of Ppy-Zn MOFs shows in presence of molecular level ordering (Fig.2). The X-ray diffraction spectrum was also used to investigate the d spacing, and peaks were observed at two theta value 18.34 (0.49 nm), 25.6 (0.35nm) and 29.5 (0.30 nm) which is similar to reported work and shows face center cubic lattice which are very different than ZnCl<sub>2</sub> XRD peak (Fig.1). The d spacing 0.35 nm consider to be distance of reaping unit of the pyrrole and 0.3 nm is inter-chain distance of Ppy in ordered structure [12].

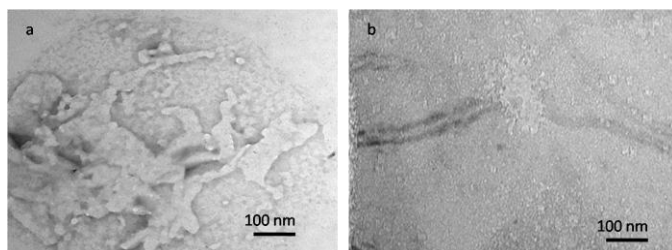


Fig. 3. Low resolution transmission electron microscope micrograph of (a) uncross-linked polypyrrole (Ppy) (stained with Iodine vapor and ((b) cross-linked Ppy with ZnCl<sub>2</sub>

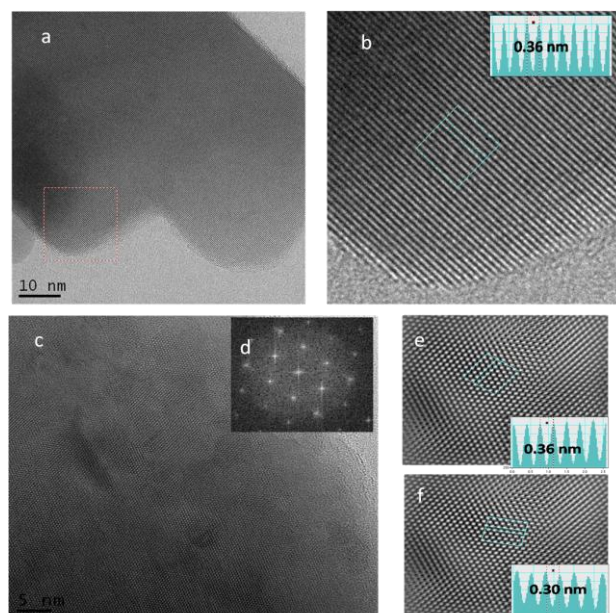


Fig.4. High resolution transmission electron microscope micrograph of (a) cross-linked polypyrrole (Ppy) at 10 nm

scale . unstained with Iodine vapor and (b) Inverse fast Fourier transform (IFFT) micrograph of the selected area of Fig.4 a , inset figure showing histogram of size distribution of lattice, (c) cross-linked polypyrrole (Ppy) at 5nm nm scale, inset figure (d) fast Fourier transform (FFT) micrograph which showing hexagonal electron diffraction, (e) and (f) shows lattice distance (inset histogram).

The morphologies of cross-linked sample characterized by high resolution transmission uncross-linked Ppy electron microscope and it compared with uncross-linked Ppy. The low resolution micrograph of uncross-linked and cross-linked Ppy shown in Fig.3a and 3b, respectively. For uncross-linked Ppy molecular ordering was not observed in transmission electron micrograph (also, no XRD peak peaks was observed in Ppy uncross-linked sample). However, very clear molecular ordering was identified in high resolution transmission electron micrograph of cross-linked Ppy sample which are very similar to XRD data. Figure 4 shows high resolution transmission electron micrograph of cross-linked Ppy. Figure 4a represent HRTEM image of the cross-linked Ppy sample with ZnCl<sub>2</sub> and it cross ponding fast Fourier transform image (IFFT) of selected area of Fig. 4a shown in Fig.4b, ordering at 0.36 nm clearly observed in Fig.4b (inset image shown histogram of size). Fig. 4c shows the image of same cross-linked film at 5 nm scale bar. inside Fig.4d show fast Fourier transform (FFT) image of electron diffraction of hexagonal geometry. The Gutan software were used to analyses the transmission electron microscope image at molecular level [10]. Fig.4e and 4f are the IFFT image of the selected area of Fig. 4c, which show lattice spacing of 0.36 and 0.30 nm, respectively which are generated from repeating unit distance and inter-chain distance, respectively, of the Ppy after cross-linking and match with reported work [12].

Electrical conductivity of the Ppy cross-linked films (110 nm thickness) was measured by the van der Pauw method. The electrical conductivity of pure Ppy observed at 0.004 S/cm as reported in Sigma Aldrich catalog (Cat No = 482552) and after cross-linking with ZnCl<sub>2</sub> its conductivity increased to 8.47 S/cm which is higher by factor of approximately 2100.

### CONCLUSIONS

In this work, we reported the simple one step process for molecular ordering in polypyrrole by cross-linking. The resulting molecularly ordered polypyrrole shown 2100 time more conductivity than uncross-linked polypyrrole. This molecular ordering method can be applied to other functional polymer to get metal organic frame work (MOF) with precise control over lattice spacing for multi applications such as electronics, photonic, magnetic and electrochemical devices.

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