Water-Controlled Synthesis of Low-Dimensional Molecular Crystals and the Fabrication of a New Water and Moisture Indicator

Zhuoyu Ji¹², Huanli Dong¹, Ming Liu², and Wenping Hu¹

¹ Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
² Key Laboratory of Nano-Fabrication and Novel Devices Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT
Arrays of low-dimensional molecular crystals of square columns (1-D) and nanolamellae (2-D) of Zn[TCNQ]₂(H₂O)₂ with large areas (up to 10⁻²⁰ cm²) have been synthesized by controlled addition of water to Zn and TCNQ. Based on the ability to accurately control the reaction, a new moisture and water indicator has been developed. The simple method, the large areas of material prepared, the fine size tuning, and the typical semiconductor behavior of the resulting low-dimensional molecular materials promise applications in molecular electronics as well as nanoelectronics. The system is an effective indicator for the detection of traces of water and moisture.

KEYWORDS
Molecular materials, molecular crystals, nanomaterials, water indicator

Molecular materials with interesting electrical, optical, and magnetic properties are a key subset of organic solids. “Hybrid” materials are of particular interest because they combine two or more properties not traditionally present in the same material, such as the combination of electrical/magnetic metal centers and conducting organic systems, i.e., metal–organic framework molecular materials. These exhibit not only intriguing architectures but also unexpected properties in asymmetric catalysis, magnetism, photoluminescence, memory, switching and so on. Moreover, materials where the metal ions bind to bi- or multi-dentate organic ligands by coordinate bonding may be synthesized from simple subunits by rapid and efficient self-assembly.

Since the first report by Dupont in the 1960s [1–10], molecular materials of metal–organic frameworks based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) have undergone a significant growth and expansion, including the development of charge-transfer complexes based on Cu and Ag [11–15]. In contrast to the abundance of investigations of the TCNQ complexes of Cu and Ag [11–15], research into to charge-transfer complexes of other transition metals.

Address correspondence to Ming Liu, liuming@ime.ac.cn; Wenping Hu, huwp@iccas.ac.cn
is still relatively underdeveloped [16–19]. Here we introduce a simple way for the controlled synthesis of low-dimensional Zn[TCNQ]2(H2O)2 based on the fine control of the addition of water to Zn and TCNQ. A new moisture and water indicator has also been developed utilizing the color change during the synthesis of Zn[TCNQ]2(H2O)2.

The controlled synthesis of Zn[TCNQ]2(H2O)2 is depicted in Fig. 1(a). First, Zn substrates were immersed into TCNQ/CH3CN solution and then one or several drops of water were added to the solution. In the absence of water, no reaction took place between Zn and TCNQ. However, as soon as water was dropped into the TCNQ solution, dark blue products were formed on the Zn substrates (Fig. 1(b)). By means of this simple controlled synthesis, products with areas varying from several mm² up to as large as 10–20 cm² could be produced. This facile method for the synthesis of molecular crystals with such large areas is an attractive way of preparing materials for application in molecular electronics.

It is interesting that the morphologies of the final products varied with the reaction time. Products with two morphologies were observed, square columns and nanolamellae, as shown in Figs. 2(a) and 2(b). The chemical composition of the columns and lamellae was determined through energy-dispersive X-ray analysis (EDX). The EDX profiles of the columns and nanolamellae exhibited similar characteristics (see Fig. S-1 in the Electronic Supplementary Material (ESM)); the peaks of C, N, O, and Zn elements were clearly identified, confirming that the products were Zn[TCNQ]x-based materials. Figure 2(c) shows a typical transmission electron microscopy (TEM) image of a square column and its corresponding selected area electron diffraction (SAED) pattern (Fig. 2(d)). The same pattern was observed for different parts of the column, indicating that the whole column was a single crystal. Similarly, the single crystal nature of the lamellae was demonstrated, as shown in Figs. 2(e) and 2(f).

X-ray photoelectron spectroscopy (XPS) data (see Fig. S-2 in the ESM) of the sub-micro columns were characterized by Zn 2P3/2 and Zn 2P1/2 peaks, with the positions of the peaks at 1023.2 eV and 1046.4 eV suggesting that the products contained Zn²⁺ ions [20]. Meanwhile, the N 1s peak appeared as a single feature at 399.05 eV, which is indicative of the presence of only one type of TCNQ [11, 21, 22]. The Fourier transform infrared (FT-IR) spectrum of the square columns is shown in Fig. 3(a). The band at 2196 cm⁻¹ occurs at lower energy than that of the

Figure 1 (a) Schematic diagram illustrating the controlled synthesis of the charge transfer complex Zn[TCNQ]2(H2O), by addition of water. (b) Controlled synthesis affords the dark blue product Zn[TCNQ]2(H2O)2 with large areas of up to 10–20 cm²

Figure 2 (a) Square columns and (b) nanolamellae of the Zn[TCNQ]2-based material. (c, e) TEM images and (d, f) SAED patterns of an individual column and lamella of the Zn[TCNQ]2-based material
infrared (IR) band of neutral TCNQ at 2224 cm\(^{-1}\), and is characteristic of the C≡N stretching mode, indicating the existence of the reduced [TCNQ]\(^-\) radical [23]. The sharp peak at 1507 cm\(^{-1}\) is further evidence of the presence of the reduced [TCNQ]\(^-\) radical [18, 24]. The distinct δ(C–H) peak at 823–824 cm\(^{-1}\) indicates the presence of [TCNQ]\(^-\) rather than the [TCNQ–TCNQ]\(^\sigma\)-dimer. The broad IR absorption band at 3440 cm\(^{-1}\), along with a weak band at ~1630 cm\(^{-1}\) indicate the presence of coordinated water molecules. The IR data strongly suggest that the products are the hydrated Zn[TCNQ]\(_2\)(H\(_2\)O)\(_2\) phase. The presence of two water molecules was further confirmed by the thermogravity analysis (TGA) data (see Fig. S-3 in the ESM). The columns lost ~7% of their mass at temperatures below 225 °C, while the lamellae lost ~7% of their mass at temperatures below 260 °C, which corresponds to the loss of two water molecules. At higher temperatures, a large change in mass occurred, indicative of decomposition via loss of TCNQ, as previously observed with M[TCNQ]\(_x\)(H\(_2\)O)\(_2\) complexes [19, 24]. The distinct difference in the TGA traces of the columns and lamellae possibly indicates that they are different phases. A careful analysis of the FT-IR spectra of the columns and lamellae was carried out in the fingerprint region 2100–2300 cm\(^{-1}\).

The columns exhibited typical peaks at 2196, 2178, and 2167 cm\(^{-1}\), while the peaks for the lamellae were located at 2219 and 2178 cm\(^{-1}\) (Inset in Fig. 3(a)), confirming the different phases of the columns and lamellae. Moreover, the different powder X-ray diffraction patterns (Fig. 3(b)) of the columns and lamellae confirmed that the columns and nanolamellae are different phases. The UV-visible absorption spectrum of the columns showed a peak at ~392 nm that can be attributed to neutral Zn[TCNQ]\(_x\)(H\(_2\)O)\(_2\) and peaks at 745 nm and 843 nm that can be assigned to the TCNQ anion radical of Zn(TCNQ)\(_2\)(H\(_2\)O)\(_2\) [25–28] (see Fig. S-4 in the ESM). Thus, the synthesis of Zn(TCNQ)\(_2\)(H\(_2\)O)\(_2\) can be depicted by the reaction

$$\text{Zn} + 2\text{TCNQ} + 2\text{H}_2\text{O} \rightarrow \text{Zn(TCNQ)}_2(\text{H}_2\text{O})_2$$

It was found that the column phase formed quickly after the zinc plate was placed into the mixed solution, while the formation of the lamellae needed much a longer time, suggesting that the columns are the kinetically favored phase I, and the lamellae are the thermodynamically favored phase II.

The two phases of Zn[TCNQ]\(_x\)(H\(_2\)O)\(_2\) are very similar to those of another charge transfer complex, CuTCNQ. However, in the formation of CuTCNQ, only Cu and TCNQ solution are involved and the reaction is difficult to control due to the rapid reaction between copper and TCNQ. In contrast, the formation of Zn[TCNQ]\(_x\)(H\(_2\)O)\(_2\) involves a ternary system, since in the absence of water no reaction takes place between Zn and TCNQ. Hence, by controlling the amount of water, the reaction between Zn and TCNQ can be finely controlled. Using limited amounts of water restricts the generation of new Zn[TCNQ]\(_x\)(H\(_2\)O)\(_2\) allowing the phase transformation to the thermodynamic product to take place. Based on such fine control of the reaction, square columns and nanolamellae could be obtained with large areas (see Fig. S-5 in the ESM). The transformation from square columns to nanolamellae is vividly depicted in Fig. 4. The transformation first occurs on the surface of the columns, and hence at the beginning of the transformation, the whole surface of the columns becomes covered with the nanolamellae, forming a hybrid of 1-D and 2-D structures.

Because the growth of the square columns and nanolamellae is based on the accurate control of
the reaction between Zn and TCNQ by addition of water, the size of the micro and nanometer sized crystals of Zn[TCNQ]2(H2O)2 can be finely tuned. For example, the width of the square columns was varied from ~100 nm to several micrometers (Figs. 5(a) and 5(b)). Similarly, the thickness of the lamellae could be tuned from ~20-30 nm to ~100-200 nm (Figs. 5(c) and 5(d)). This ability to fine tune the size of 1-D and 2-D nanostructures of molecular materials by the control of reaction conditions is attractive in terms of applications of the materials in nanoelectronics. Although nanoelectronics has attracted worldwide attention and undergone rapid development, despite thousands of nanostructures and particles having been synthesized and applied in electronics, it is still a great challenge to control the size and patterning of nanostructures. Here, we have demonstrated a simple method to achieve such control by employing a ternary reaction system.

The formation mechanism of the square columns of Zn[TCNQ]2(H2O)2 is different from that of the square columns of the charge transfer complex CuTCNQ. For CuTCNQ, the formation process of its columns can be depicted by a “coalescence” mechanism. The primary product is always the kinetic product of nanorods, and the nanorods tend to aggregate with each other, so that they quickly evolve into “square columns” with widths of several hundreds of nanometers [29]. However, for Zn[TCNQ]2(H2O)2 the primary products seem to be amorphous square columns (see Fig. S-6 in the ESM) which subsequently evolve into crystalline square columns.

It is important to understand the electrical properties of molecular crystals because of their potential application in devices. A series of devices based on an individual single crystalline column of Zn[TCNQ]2(H2O)2 were fabricated with a coplanar electrode geometry. Single crystalline square columns were employed because single crystals of a molecular material are better able to reveal the intrinsic properties of the material and open up prospects for the fabrication of high quality devices. A schematic diagram of the device fabrication process is given in the top left inset of Fig. 6. First, an individual Zn[TCNQ]2(H2O)2 column was moved onto a Si/SiO2 (300 nm) substrate by mechanical probes [30]. Second, a micro Au wire was used as the mask for the deposition of Au electrodes on the crystal by thermal evaporation (as shown in the top left inset of Fig. 6). With this method a gap of ~20 μm was produced between the two electrodes (as shown in the bottom right inset of Fig. 6). A typical current voltage (I–V) plot of the
single crystalline column is shown in Fig. 6. The highly reproducible, symmetrical $I$-$V$ characteristics of the devices suggest symmetrical contacts between the column and electrodes. Two separate voltage regions were observed, with a nearly ohmic $I$-$V$ dependence at low voltage and a rough $I$-$V^2$ dependence at higher voltages, indicating a space charge limited current (SCLC) in the crystal [31]. Moreover, it is interesting to note that all the devices exhibited similar semiconductor behavior, and even when higher voltages were applied to the devices until they broke, no switching phenomena were observed. The $I$-$V$ characteristics of the nanolamellae were similar to those of the square columns. Therefore, it is reasonable to conclude that Zn[TCNQ]$_2$(H$_2$O)$_2$ is not a switching material, in contrast to CuTCNQ which shows high resistance under low voltage bias (“OFF” state) and high conductivity under high voltage bias (“ON” state). However, the typical semiconductor behavior of the single crystalline products of square columns and nanolamellae suggested potential applications of the 1-D and 2-D nanostructures of Zn[TCNQ]$_2$(H$_2$O)$_2$.

An important application of Zn[TCNQ]$_2$(H$_2$O)$_2$ is based on the characteristic of its water-controlled synthesis. Traces of water will result in the generation of the dark blue molecular material. Hence, the appearance of the dark blue Zn[TCNQ]$_2$(H$_2$O)$_2$, i.e., the color change of the Zn substrate, can be used as an indicator to monitor the appearance of water, such as in inspection of traces of water or leak hunting. As preliminary experimental results, the dependence between the color of the Zn substrate and the amount of water in the reaction of Zn and TCNQ to give Zn[TCNQ]$_2$(H$_2$O)$_2$ is depicted in Fig. 7(a). When different amounts of water were added to the TCNQ solution, the colours of the substrates were tuned because of the generation of Zn[TCNQ]$_2$(H$_2$O)$_2$ on the substrates. Without water added to the solution, no products appear. Hence, the appearance of Zn[TCNQ]$_2$(H$_2$O)$_2$ can be used as an effective indicator of the presence of traces of water.

The appearance of Zn[TCNQ]$_2$(H$_2$O)$_2$ can also be used as an indicator to monitor the presence of moisture. With different amounts of moisture, the amount of Zn[TCNQ]$_2$(H$_2$O)$_2$ generated on the substrates will be different, and consequently the colors of substrates will be tuned. Simple color observation can be used to monitor the amount of moisture. For example, it was found that the colors of co-deposited films of TCNQ:Zn (5:1) (50 nm), or films produced by alternate deposition of Zn (1 nm)/TCNQ (5 nm) (with 10 repetitions), varied with moisture

![Figure 6](image_url)  
**Figure 6** $I$-$V$ characteristics of a single column. The insets show a schematic illustration of the device fabrication process and the SEM image of an individual column device.

![Figure 7](image_url)  
**Figure 7** Fabrication of the new water and moisture indicator based on the reaction of Zn, TCNQ, and traces of water to afford Zn[TCNQ]$_2$(H$_2$O)$_2$; the color change is an efficient way of detecting the presence of water and moisture. All samples involve the same reaction time of 1 min.
content (the simulated moisture was obtained by adding different numbers of drops of water into a hermetically sealed bottle as shown in Fig. 7(b) (the volume of the bottle was 12 mL and one drop of water was around 5 μL).

In summary, low-dimensional molecular crystallites of square columns and nanolamellae of Zn[TCNQ]2(H2O)2 with large areas (from several mm² to 10–20 cm²) have been synthesized by controlled addition of water. The square columns of Zn[TCNQ]2(H2O)2 were identified as the kinetic product phase I, and the nanolamellae were the thermodynamic product phase II. Based on the accurate control of the synthesis of Zn[TCNQ]2(H2O)2 by reaction between Zn and TCNQ induced by addition of water, i) the transformation mechanism from square columns to nanolamellae was clearly monitored, ii) the size of the micro and nanometer sized crystals of Zn[TCNQ]2(H2O)2 can be finely tuned, iii) and a new moisture and water indicator has been developed. Devices based on an individual square column or nanolamella demonstrated the typical semiconductor behavior of the single crystalline products. This simple method for the large scale synthesis, the ability to fine tune the size, and the typical semiconductor behavior of the low-dimensional molecular materials are attractive in terms of developing new materials for molecular electronics and nanoelectronics. The new water or moisture indicator can be used for the inspection of water and moisture, such as monitoring the presence of traces of water, leak hunting or moisture monitoring.

Experimental

The zinc plates were successively cleaned with pure water, ethanol, acetone, dilute HCl, and pure water. After cleaning, the zinc plates were immersed into a TCNQ/acetonitrile solution, and then drops of water were carefully added. Finally, the zinc plates were removed from the TCNQ solution and gently washed with acetonitrile to remove any excess TCNQ, followed by drying under a stream of N2.

The Zn[TCNQ]2(H2O)2 products were characterized by UV-visible spectroscopy (U3010), FT-IR (PE2000), XPS (ESCALab220I-XL), X-ray diffraction (XRD) (D/max2500), scanning electron microscope (SEM) (Hitachi S-4300 SE), and TEM (JEOL 2010). A Keithley 4200 SCS Semiconductor Characterization System was used to measure the current–voltage characteristics of the nanorods.

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Electronic Supplementary Material: Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s12274-009-9084-x and is accessible free of charge. It contains further experimental details, information about the fabrication of low dimensional molecular crystals, including typical SEM images and the corresponding energy-dispersive X-ray (EDX) traces of the columns and lamellae, XPS data for the sub-micro columns, TGA traces for the square micro columns, the UV-visible spectrum of the square columns, large area images of square columns and nanolamellae, and the mechanism of formation of square columns of Zn[TCNQ]2(H2O)2.

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