Synthesis of Fe(II) Terpyridine Complex Nanosheet

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Abstract: Fe(II) terpyridine complex nanosheet was synthesized using ligand: 1,3,5-Tris[4-(2,2':6',2''-terpyridin-4'-yl)phenyl]benzene, (tpy)3, and Fe(II) supplying salt: Fe(BF4)2·6H2O. A liquid-liquid interfacial polymerization was employed, giving thick nanosheets. The product was then subjected to X-ray photoelectron spectroscopy (XPS), IR, Elemental Analysis (EA), Cyclic Voltammetry (CV), as well as Scanning Electron Microscope (SEM) for confirming the structure.

Keywords: Fe(II) terpyridine complex nanosheet • (tpy)3 • liquid-liquid interfacial polymerization • XPS • IR • EA • CV • SEM.

INTRODUCTION

Nanosheets are novel 2D planar materials with several nanometers thickness. Because of their great potentials for electronic devices, such as FET and capacitors, they have been of increasing interest during the last few decades. In our lab, metalladithiolene nanosheet has been studied by Kambe-san and Hoshiko-san before. Using similar idea and method, the aim of this program is to synthesis Fe(II) terpyridine complex nanosheet and confirm the structure.

In the study, we used 1,3,5-Tris[4-(2,2':6',2''-terpyridin-4'-yl)phenyl]benzene, (tpy)3, as ligand (Figure 1).

Terpyridine was employed as the base of ligand because of the distinct photophysical, electro-chemical and magnetic properties of 2,2':6',2''-terpyridine-complex structures. Meanwhile structure (tpy)3 was employed for it has less hindrance than the hexafunctional terpyridine-based symmetric monomer, (tpy)6, reported before (Figure 2).[1]
Beyond that, this Fe(II) terpyridine complex nanosheet (Figure 3) was prepared under air, while the metalladithiolene nanosheet mentioned above was prepared only under inert atmosphere.

RESULTS

Preparation of the \((tpy)_3\) ligand

We synthesized the ligand \((tpy)_3\) following the steps from literature (Scheme 1).\(^2\)

1,3,5-tribromobenzene, tpy-Bneo, [Pd(PPh\(_3\))]\(_4\) and aqueous Na\(_2\)CO\(_3\) were dissolved in THF at 85 °C in a Schlenk flask under an atmosphere of nitrogen. The product precipitated from the mixture after 20.5 h and was collected through filtration on a Kiriyama funnel. Next, the solid was washed with THF, water, Et\(_2\)O, and then vacuum dried. The yield was 38.02%

Later, the structure of \((tpy)_3\) was confirmed by \(^1\)HNMR\(^3\) and ESI-TOF-MS.

Synthesis of the nanosheet

Liquid-liquid interfacial synthesis was employed for synthesizing (Figure 4). Under ambient condition, three layers of liquid were prepared.

In the organic phase, \((tpy)_3\) was dissolved in dichloromethane (1.0 mM). Pure water was gently added afterwards as a buffer, providing a calm interface for polymerization. Fe(II) salt Fe(BF\(_4\))\(_2\)-6H\(_2\)O (252.8 mM) was supplied from the aqueous phase. Meanwhile (BF\(_4\))\(^-\) was used as an anion to balance the positive charge of the nanosheet. The condition of the interface is essential in this situation. The existence of little particles or any other disturbance of the interface would lead to a failure of synthesizing.

Reproducibility was proved by making 24 more bottles under the same condition.

Normally, synthesizing could be observed after about 30 minutes of adding Fe(BF\(_4\))\(_2\)-6H\(_2\)O solution. All nanosheets were collected through filtration.

![Figure 3 Chemical structure of the aimed Fe(II) terpyridine complex nanosheet.](image_url)

![Figure 4 A photo of the nanosheet, taken 4 days after synthesizing. A syringe was used for filtration and transfer of dichloromethane solution for the left bottle.](image_url)

![Scheme 1 Synthesis of the ligand \((tpy)_3\) according to literature.](image_url)
Confirming the structure

Upon confirming the structure, the nanosheet was subjected to X-ray photoelectron spectroscopy (XPS), IR, Elemental Analysis (EA), Cyclic Voltammetry (CV), as well as Scanning Electron Microscope (SEM) measurements.

X-ray photoelectron spectroscopy (XPS)

The results of XPS were shown in figure 5. (Tpy)$_3$, nanosheet, and [Fe(tpy)$_2$](BF$_4$)$_2$ complex were used as samples in XPS measurement.

The fact that peaks of N 1s shifted slightly to the left from (tpy)$_3$ to nanosheet and then to [Fe(tpy)$_2$](BF$_4$)$_2$ complex, together with the peak positions of Fe 2p spectra, suggests the formation of Fe(tpy)$_2$ structure (Figure 6). In the case of nanosheet, the spectrum of N-1s is the result of two peaks overlapping, indicating that some ligand failed to react. At last, spectra of B 1s and F 1s proved the anion to be (BF$_4$)$_-$, also indicating some unreacted ligand.

IR spectra

Figure 7 is the IR spectra of (tpy)$_3$, nanosheet, terpyridine as well as [Fe(tpy)$_2$](BF$_4$)$_2$ complex in KBr pellets. Vibration of the anion (BF$_4$)$^-$ was observed around 1100 cm$^{-1}$, while typical pyridine valence vibrations around 800 cm$^{-1}$ and 1600 cm$^{-1}$ were also detected.

Figure 6 Chemical structure of Fe(tpy)$_2$. 
Furthermore, the absorbance around 1600 cm\(^{-1}\) moved to the left from (tpy)\(_3\) to nanosheet slightly, supporting the formation of the nanosheet.

**Elemental Analysis**

Figure 8 is the chemical structure of the nanosheet. The calculated formula from this structure is: \((\text{C}_{69}\text{H}_{45}\text{N}_{9})\text{Fe}_{1.5}(\text{BF}_4)_3\), and thus giving the result of calculation: C: 61.63\%; H: 3.38\%; N: 9.38\%.

Table 1 is the results of Elemental Analysis. The difference between calculation and measurement may be caused by water, impurity or insufficient sample.

<table>
<thead>
<tr>
<th></th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
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<tbody>
<tr>
<td>CAL</td>
<td>61.63</td>
<td>3.38</td>
<td>9.38</td>
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<tr>
<td>MER(0.8187mg)</td>
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<tr>
<td>MER(mean)</td>
<td>55.67</td>
<td>4.51</td>
<td>6.80</td>
</tr>
</tbody>
</table>

Table 1 Results of Elemental Analysis. CAL means calculation. MER means measurement. The difference between calculation and measurement may be caused by water, impurity or insufficient sample.

**Cyclic Voltammetry**

Electrochemical measurement of nanosheet was carried out later in a standard one compartment cell. Upon preparing the sample, nanosheet was first dispersed as little particles in dichloromethane, and then transferred to the HOPG electrode surface. Using this HOPG as working electrode, platinum-wire electrode as counter electrode, \(\text{Ag}^+/\text{Ag}\) reference electrode (10 mM...
AgClO₄ and 0.1 mM n-Bu₄NCIO₄ (TBAP) in MeCN solution) as reference electrode, and 0.84 M dichloromethane solution of TBAP as electrolyte solution, Cyclic Voltammetry, as expected, showed a good result. Only one redox couple derived from Fe³⁺/Fe²⁺ in bis(terpyridine) complex was observed beautifully at E° = 0.83 V vs. Ag/Ag⁺, suggesting an almost completely reversible reaction. The positions of these two peaks, re-proved the formation of the nanosheet. This result disproved the existence of any redox-active impurity such as Fe(BF₄)₂.

**Scanning Electron Microscope (SEM)**

Scanning Electron Microscope (SEM) was applied trying to see the nanosheet directly (Figure 9 and Figure 10). From the image of SEM, one can see that the surface of nanosheet is very smooth, much smoother than that of the tape. On Figure 9, it is clear that some pieces of the nanosheet are transparent, while others are not, which suggests that nanosheets may be of different thickness.

Meanwhile, some unknown spots are observed on the SEM images. They might be little pieces of the sheet, dust from air, or particles or molecules of impurities.

![Figure 9 SEM image of the nanosheet. 15.0 kV × 350. Dots represent elements: White: C ; Red: N ; Green: Fe.](image1)

![Figure 10 SEM images of the nanosheet, 15 kV; magnification, from left to right: × 350, × 1,000, × 10,000.](image2)
DISCUSSION AND PERSPECTIVE

Considering the results of different measurements above, we could say that we have successfully synthesized Fe(II) terpyridine complex nanosheet. However, Elemental Analysis should be conducted again, together with some other measurements.

A main difference of structure between this nanosheet and the metalladithiolene nanosheet studied by Kambe-san and Hoshiko-san before is that the latter one has a totally flat surface, while the former one shows vertical structure between two terpyridine structures at every Fe spot. To prove this structure directly, one may consider getting the single crystal of the nanosheet, and then try X-ray diffraction.

Furthermore, one may try to create nanosheet of atomic thickness, employing gas-liquid interface reaction Kambe-san used, or Langmuir Blodgett method Hoshiko-san tried before. After getting the nanosheet of atomic thickness, it would be very interesting to determine the electronic property. Our lab has done a lot of work concerning the electric behavior of nano-wires, in which electro was conducted one way through. However, in the case of a 2D sheet, different metal cores may show different abilities of conducting, so as to exhibit an interesting result of conducting overall.

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REFERENCE