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SYNTHESIS OF PORPHYRIN-POLYTHIOPHENE NANOTUBES AND THEIR ZINC COMPLEX AND SILVER NANOPARTICLE COMPOSITES

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Abstract – The template-based electropolymerization of terthienyl-porphyrin, **1**, and its zinc porphyrin, Zn-**1**, in a nanoporous alumina template produced the corresponding new porphyrin nanotubes, poly-**1** NTs and poly-Zn-**1** NTs, respectively. The encapsulation of silver nanoparticles into the inner cavity of the poly-**1** NTs provides the silver nanoparticle-porphyrin hybrid NTs.

There has been significant interest in the synthesis and functionalization of porphyrins and their transition metal complexes (metalloporphyrins) due to their unique electronic, optical and structural properties, narrow emission bands with a broad absorption wavelength and photostability.[1] Their potential applications have been intensively investigated in many science and technology areas such as chemosensors, solar energy cells, electrochromic agents, and photodynamic therapy. In particularly, porphyrins are the preferable photosensitizers for utilizing solar energy.

Recently, much more research interest has focused on nanotubes (NTs) formed from a variety of materials.[2] It is advantageous or required to modify their nanotubes by physical or chemical methods to optimize their use in many applications. There are fewer reports on the synthesis of porphyrin NTs, in which their nanotubes were obtained by the vaporization-condensation-recrystallization process of the metal-free 5,10,15,20-tetra(4-pyridyl)porphyrin and by ionic self-assembly of two oppositely charged porphyrins in an aqueous solution.[3,4] However, fabricating porphyrin NTs is still a great challenge. We previously reported the synthesis of functional polythiophene NTs by the template-based electropolymerization of functional thiophenes in a nanoporous alumina membrane as the template.[5] For example, a new plasmonic hybrid nanotube as a photo-antenna material of fullerene C_{60}-polythiophene gold nanoparticles was synthesized via the template-based electrocopolymerization of terthiophene-linked fullerene C_{60} and terthiophene-modified gold nanoparticles using a nanoporous alumina membrane as the template.[6]

Dedicated with respect to Professor Dr. M. Shibasaki on the occasion of his 70th birthday

The combination of porphyrin and polythiophene in the electrochemically modified electrode is one of the useful systems for photocurrent generation and solar cells.[7] Polythiophene as one of the classical and excellent donor materials for use in photovoltaic devices has attracted extensive attention. No clear-cut example of the nanotubes consisting of porphyrin and polythiophene is currently known. This communication reports the template-based synthesis of porphyrin-polythiophene NTs and their zinc complex, and the confinement of silver nanoparticles in the inner cavity of the porphyrin-polythiophene NTs.

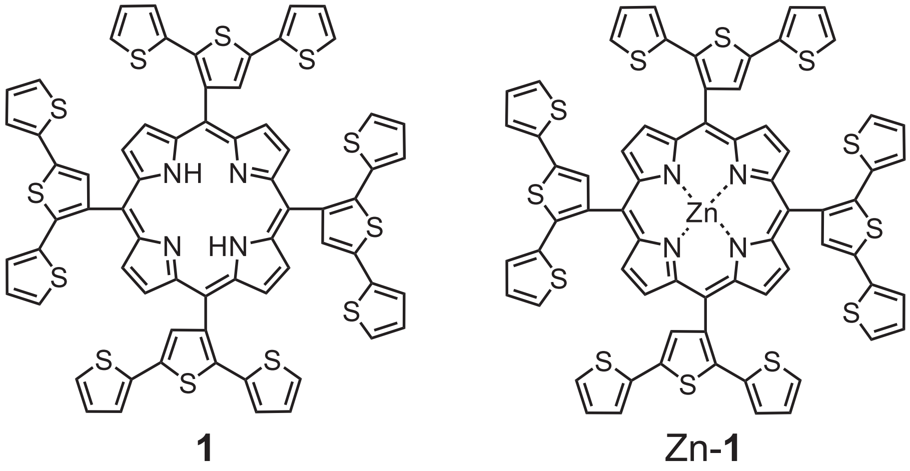

Figure 1. Structures of **1** and Zn-**1**

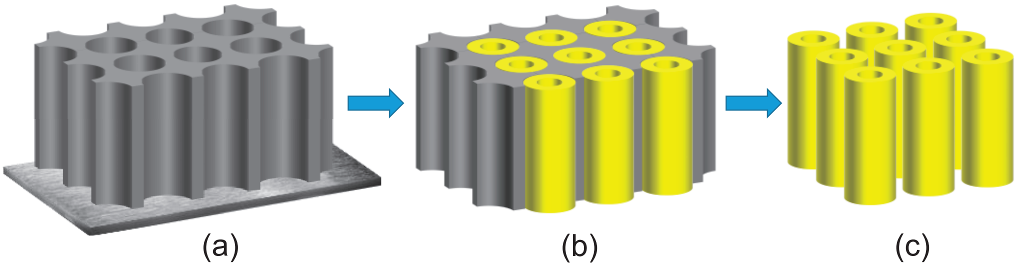

Figure 2. Template-based synthesis of the porphyrin NTs: (a) bare porous alumina membrane (AM). (b) deposition of the porphyrin NTs formed by the template-based electropolymerization of **1** or Zn-**1** leads to poly-**1**-NTs-AM or poly-Zn-**1**-NTs-AM as a polymer nanotube membrane. (c) polymer nanotubes, poly-**1** NTs or poly-Zn-**1** NTs, are isolated by dissolution of the porous alumina template.

In order to synthesize the porphyrin NTs of **1**[8] by electrochemical polymerization, the electropolymerization of **1** was investigated in the absence or in the presence of a porous alumina membrane. The electrochemical property of **1** was studied by cyclic voltammetry. The cyclic voltammogram (CV) of **1** in 0.1 M Bu_4NPF_6-CH_2Cl_2 at a glassy carbon electrode showed an irreversible oxidation peak at $E = +0.68$ V (vs. Ag/0.1 M $AgNO_3$) due to oxidation of the terthiophene unit (Figure 3a), and two reversible redox peaks at $E_{1/2} = -1.37$ and -1.75 V (vs. Ag/0.1 M $AgNO_3$) due to the porphyrin ring (Figure 3b). In the following scans, an increase in the anodic/cathodic peaks of **1** was noted as an indication of the polymer growth (Figure 3a). Many scans of the poly-**1** film-modified electrode can be repeated without any change in the voltammetric wave.

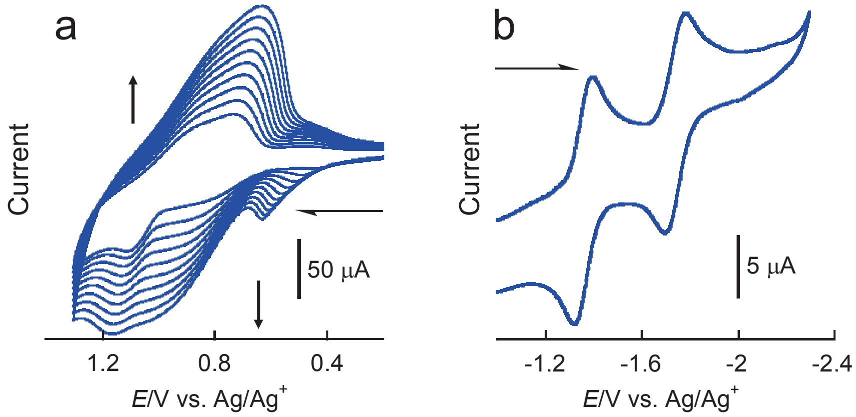

Figure 3. Cyclic voltammograms of 1 mM **1** on a GC electrode in 0.1 M Bu_4NPF_6-CH_2Cl_2: (a) multiple scans and (b) first scan. Scan rate, 100 mV/s.

A typical procedure for the template-based synthesis of the poly-**1** NTs is as follows. The electropolymerization was performed by attaching the porous alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode. Another Pt electrode was used as the counter electrode and Ag/0.1 M $AgNO_3$ was used as the reference electrode. The electrolysis solution contained the porphyrin **1** (6.5 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2. A voltage of +1.04 V (*vs*. Ag/0.1 M $AgNO_3$) was applied for 60 min. After the template-based electropolymerization, removal of the porous alumina membranes with 1 M NaOH led to the release of the porphyrin polythiophene NTs (ploy-**1** NTs) (yield = 0.8 mg).

The poly-**1** NTs were characterized by UV-vis spectroscopy, scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray (EDX) spectra. The UV-vis spectrum of **1** in DMSO showed absorptions at 368 nm due to the terthiophene unit, at 425 nm due to the Soret band, and weak absorptions at around 525 nm~650 nm due to the Q-band (Figure 4a), while the UV-vis spectrum of the poly-**1** NTs in DMSO exhibited absorption at 439 nm corresponding to the Soret band and broad absorptions at 500 nm~700 nm due to the polythiophene and the Q-band (Figure 4b). Figure 5a shows a typical SEM image of the poly-**1** NTs nanotube arrays. It can be clearly seen that an ordered array of the NTs with a uniform diameter is formed. The hollow nature of the nanotubes is also confirmed by the STEM image shown in Figure 5b. The STEM image of the poly-**1** NTs showed an outer diameter of about 250 nm which corresponds to the pore diameter of the porous alumina membrane and the inner diameter of 190 nm. The energy-dispersive spectroscopy line scan of the poly-**1** NTs showed that the orange intensity is from nitrogen (Figure 5c), while the yellow intensity is from sulfur (Figure 5d). These data indicate the formation of the porphyrin-polythiophne NTs.

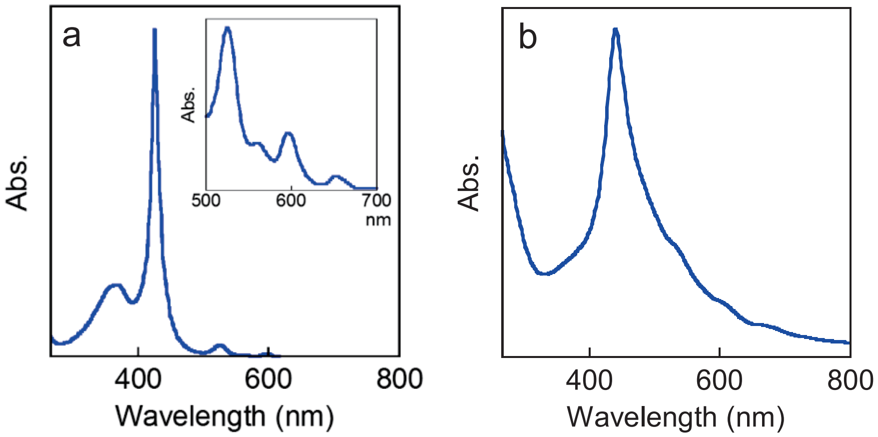

Figure 4. UV-vis spectra of (a) **1** in DMSO and (b) poly-**1** NTs in DMSO

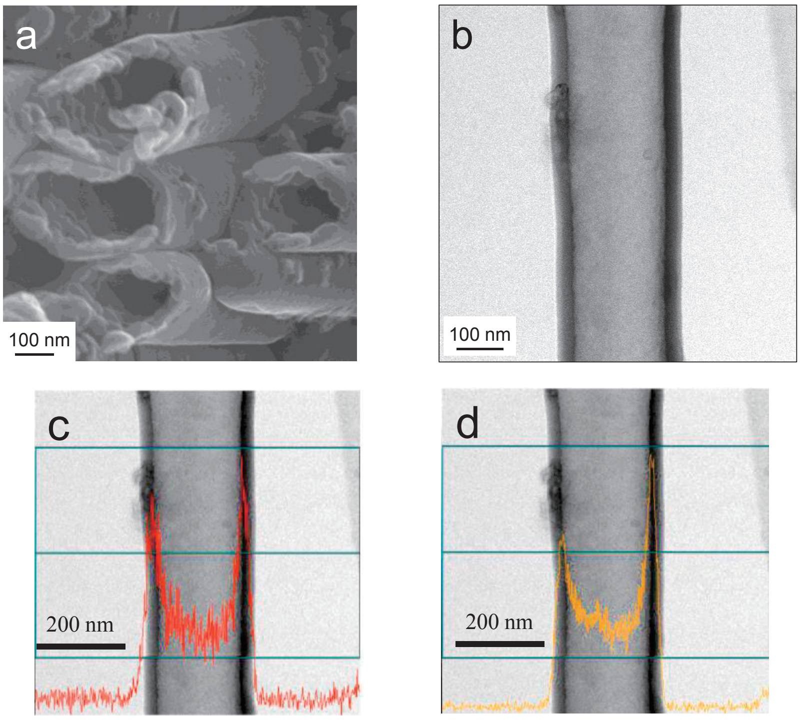

Figure 5. Poly-**1** NTs: (a) SEM image, (b) STEM image, and (c, d) EDX line scans

We have succeeded in the preparation of metallo-porphyrin polymer nanotubes without desorption of the metal from the metallo-porphyrin by the template-based electropolymerization method. The template-based synthesis of Zn-**1**[7,8] in a nanoporous alumina membrane formed the corresponding polymer nanotubes (poly-Zn-**1** NTs). The zinc porphyrin complex, Zn-**1**, was characterized by X-ray photoelectron spectroscopy (XPS) and UV-vis spectroscopy. The XPS spectrum of Zn-**1** displayed the

Zn 2p binding energies at 1021 ($2p_{3/2}$) and 1044 ($2p_{1/2}$) eV, corresponding to the zinc metal (Figure 6a). The UV-vis spectrum of Zn-**1** in CH_2Cl_2 showed the formation of the zinc complex of the porphyrin which is consistent with that of the reported zinc-porphyrin[7,8] (Figure 6b). Figure 6c shows the UV-vis spectrum of the poly-Zn-**1** NTs. Figure 7a shows an SEM image of the poly-Zn-**1** NTs, which were grown using the porous alumina template; most of them having outer diameters of about 200 nm. The EDX spectrum of the poly-Zn-**1** NTs revealed the presence of zinc, nitrogen, and sulfur (Figure 7b). These results clearly indicated that the electropolymerization of Zn-**1** in a porous alumina template led to the formation of the nanotube composites consisting of zinc, porphyrin, and polythiophene as constituents of the nanotubes.

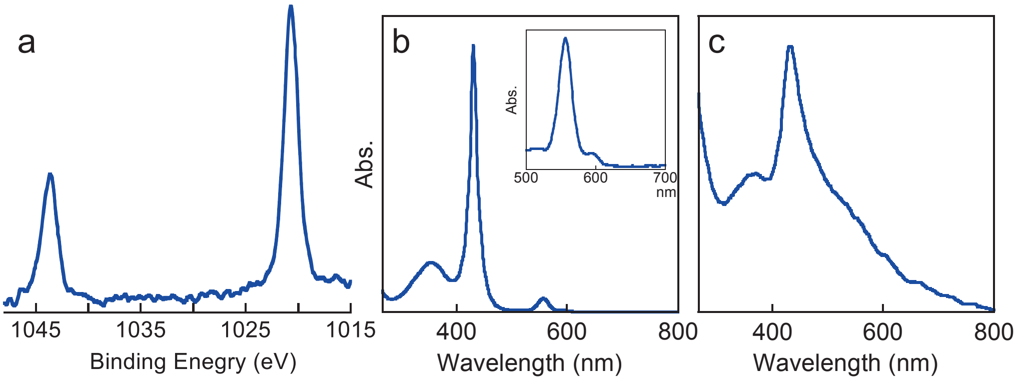

Figure 6. (a) XPS spectrum of Zn-**1**, (b) UV-vis spectrum of Zn-**1** in CH_2Cl_2, (c) UV-vis spectrum of poly-Zn-**1** NTs in CH_2Cl_2

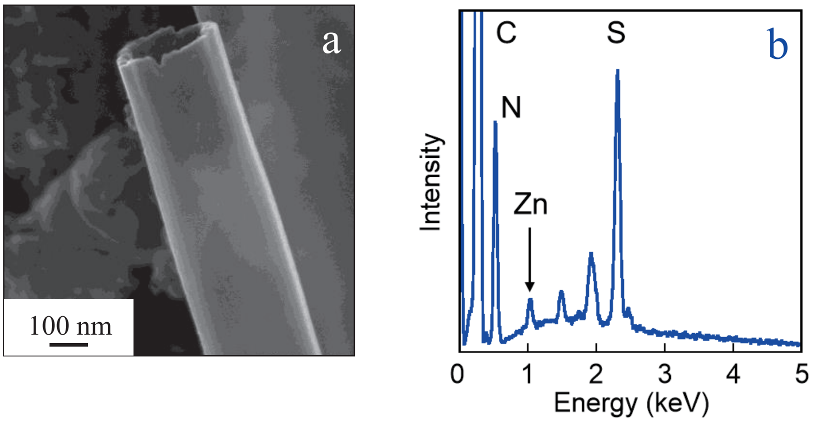

Figure 7. Poly-Zn-**1** NTs: (a) SEM image and (b) EDX spectrum

The plasmonic silver nanoparticles can be incorporated into the poly-**1** NTs by the following method. The oleylamine-stabilized silver nanoparticles were prepared according to a reported method.[9] The oleylamine-stabilized silver nanoparticles were added to the poly-**1** NTs deposited-alumina membrane (poly-**1**-NTs-AM) (Figure 2b) followed by dissolution of the porous alumina membrane upon treatment with 1 M NaOH to give the silver nanoparticles confined in the nanopores of the poly-**1** NTs (Ag NP-poly-**1** NTs) as evidenced from the TEM image (Figure 8a), the dark-field scanning transmission electron microscopy (STEM) (Figure 8b) and STEM-EDX mapping analysis (Figure 8c).

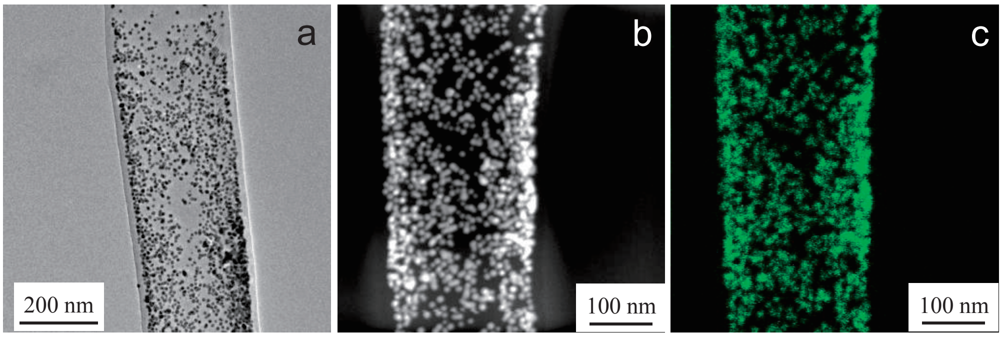

Figure 8. Ag NP-poly-**1** NTs: (a) TEM image, (b) STEM image, and (c) EDX mapping of the silver

In summary, the porphyrin NTs were synthesized by the template-based electropolymerization of terthiophene-linked porphyrin in a nanoporous alumina membrane. We have performed the synthesis of the composite nanotubes consisting of a zinc complex and silver nanoparticles. A study of the photocatalytic properties of the new composite porphyrin nanotubes is currently under way.

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