donated from the 32-electron heterocluster to provide the closed-shell eight-electron configuration of the phosphorus atoms. This leaves eight electrons for internal bonding and is consistent with four 3c–2e bonds in the (distorted) tetrahedral cluster.

The only previously reported example of a mixed polyphosphide with a transition/post-transition metal heterocluster is Cu_4SnP_{10}.[10] Its crystal structure also contains distorted tetrahedral units (towards pyramidal Cu_3Sn). However, the phosphorus partial structure consists of discrete adamantane-like P_{10} cages, which are interconnected by Cu_3Sn heteroclusters and additional copper atoms. The discovery of Ag_3SnP_7 indicates that the nature of the metal atoms may play a crucial role in defining the structure of phosphorus structural fragments and their interconnection.

Experimental Section

Ag_3SnP_7: silver, tin, and red phosphorus in the stoichiometric ratio were used as starting materials (1 g in total). A few crystals of SnI_4 (ca. 0.01 g) were added to the mixture to provide effective vapor-phase transport. Annealing twice in an evacuated silica ampoule (inner diameter 6 mm; length 5 cm; 823 K for 7 d, slow cooling to ambient temperature) with intermediate grinding of the products gave a black monophase product. No impurities were detected by X-ray diffraction (as a small amount of SnI_4 was added to the original mixture this observation means that formation of iodine-containing substances is negligible). All attempts to synthesize Ag_3SnP_7 without the use of SnI_4 led to low yields.

A single crystal for the X-ray structure determination was found among the products of annealing a mixture of tin, silver, tin(IV) iodide, and red phosphorus in the ratio Sn:Ag:SnI_4:P = 17.5:4.5:2:22 (conditions were as above).

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[3] Crystal structure of Ag_3SnP_7: monoclinic, space group $P2_1/m$ (no. 11), $a = 6.360(1)$, $b = 11.071(2)$, $c = 6.518(1)$ Å, $\beta = 108.17(1)^\circ$, $V = 436.1(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 5.020\ g\,cm^{-3}$. 1430 reflections, 1329 of which were independent ($R_{int} = 0.0285$), $T = 294$ K, $\omega/2\theta$ scans, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $2\theta_{max} = 60.0^\circ$, crystal dimensions $0.12 \times 0.05 \times 0.05\ mm^3$, semiempirical absorption correction (ψ scans of seven reflections, min./max. transmission: 0.6936/0.9969, $\mu = 10.668\ mm^{-1}$). Structure solution: direct methods (SHELXS-86),[11a] refinement against F^2 (1186 reflections with $F > 4\sigma(F)$) by full-matrix methods (SHELXL-97)[11b] with 56 free parameters; $R1 = 0.0425$, $wR2 = 0.0930$; max./min. residual electron density: $3.775/-2.127\ e\,Å^{-3}$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411041.

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Fixation of Dinitrogen to a Mesoscale Solid Salt Using a Titanium Oxide/Conducting Polymer System**

Katsuyoshi Hoshino,* Masaki Inui, Takashi Kitamura, and Hiroshi Kokado

Since Schrauzer and Guth[1] reported the photocatalytic reduction of dinitrogen on titanium oxides under mild conditions, efforts have been devoted to prepare more effective catalysts and to understand the reaction mechanism;[2] such N_2 fixation under mild conditions is an important goal of many research groups.[3] However, the products of this reaction are gaseous ammonia (major) and hydrazine (trace); solid products which are easily isolated, manipulated, and characterized, have not been synthesized by this process. Herein, we describe a system to fix N_2 as an ammonium perchlorate salt, which has a structure of mesoscale needles. Dinitrogen fixation to this salt occurs upon white-light irradiation of a titanium oxide/conducting polymer system under ambient temperature and pressure conditions. The needles grow from the conducting polymer matrix and increase in size and abundance with irradiation time and intensity. The formation of such structures as a result of N_2 fixation is explained on the basis of ammonia synthesis on the oxide coupled with perchlorate dedoping of the conducting polymer.

The system used here is a composite of poly(3-methylthiophene) (P3MeT) and a titanium oxide, both of which were prepared electrochemically. A solution of 3-methylthiophene (3MeT, 0.08 M) and tetrabutylammonium perchlorate ($TBA^+ClO_4^-$, 0.1 M) in dichloromethane was subjected to galvanostatic electrooxidation at a temperature T of 13 °C for a time t of 400 s with a constant current density j of $1.5\ mA\,cm^{-2}$ in a one-compartment cell.[4] The cell was equipped with a titanium oxide anode ($2.14\ cm^2$) and a Pt plate cathode ($2.14\ cm^2$). An electrochemically synthesized titanium oxide (ETO) layer on the anode was formed by the anodic oxidation[5] of a Ti plate in a CH_2Cl_2 solution containing 0.1 M of $TBA^+ClO_4^-$ under galvanostatic conditions of $j = 0.7\ mA\,cm^{-2}$, $T = 20$ °C, and $t = 970$ s. The Ti plate (> 99.5 % purity) contained impurities such as Fe (0.250 %), K (0.013 %), O (0.200 %), and N (0.050 %); prior to the anodic oxidation the plate was degreased and etched by dipping in aqueous HF (5 %, 5 min) and then in an HF (1 %)/HNO_3 (3 %)/H_2O_2 (10 %) mixture for 30 s. In addition, prior to the deposition of P3MeT, the ETO layer was washed in trichloro-

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[*] Prof. Dr. K. Hoshino, M. Inui, Prof. Dr. T. Kitamura,
Prof. Dr. H. Kokado
Faculty of Engineering
Chiba University
1-33 Yayoi, Inage, Chiba 263-8522 (Japan)
Fax: (+81) 43-290-3490
E-mail: hoshino@image.tp.chiba-u.ac.jp

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ethylene, acetone, and ethanol with sonication. After washing, the ETO-coated anode appear purplish-blue. After the electrooxidation, the plate appeared deep green, and deposition of the P3MeT (2.5 μm thick) covered about 70% of the surface. The surface and deposition was repeatedly washed with CH_2Cl_2 and dried. The molar ratio of ClO_4^- to 3MeT was 0.16, as determined by energy-dispersive X-ray analysis coupled with a scanning electron microscope (SEM). Specimens for electron micrography were collected from the anode and characterized by SEM.

Photoirradiation experiments in a moist dinitrogen or moist argon atmosphere were carried out in a sealed box ("closed system"; fabricated from acrylic plates 10 mm thick with an inner volume of $110 \times 110 \times 80\ mm^3$) equipped with stainless steel needle valves through which the passage of air and desired gases could be controlled. Illumination of samples within this closed system was made through a quartz window (70 × 70 × 3 mm) in the box. Experiments in air were conducted in a second, wooden box ("flow system"; inner volume 600 × 500 × 900 mm; approximately 20°C and 40% relative humidity) to prevent the samples being contaminated with dust. The results from the flow system were identical to those done in the air-filled closed system and in the open air.

Immediately after the P3MeT deposition, no needle-shaped crystals could be found within the deposit (Figure 1a). However, crystals were recognized within the deposit after 7 days (Figure 1b). Unless otherwise noted, the deposits were stored in contact with the ETO layer under an ambient atmosphere and white-light irradiation (300 lx, Hitachi FL20SSN fluorescent lamp). After 45 days, the density and length of the needles increased (Figure 1c). These needle structures are morphologically intriguing but the fundamental significance lies in their chemical structure. Fourier transform infrared (FTIR) spectra taken from individual needles were the same in shape and peak positions as that of $NH_4^+ClO_4^-$, which is well known from its use as a solid rocket propellant.[6] The FTIR spectrum of a needle-rich sample (taken after 180 days of white-light irradiation) was composed of the superposition of absorption bands for an undoped P3MeT[7] and those of $NH_4^+ClO_4^-$, and was entirely different from that of a needle-free sample, which was identified as a ClO_4^--doped P3MeT.[7] This result provides an important clue to the solid-state reactions during needle growth: The ClO_4^- proceeds to eliminate from the ClO_4^--doped P3MeT deposit and forms the anionic component of the needle formations. This is consistent with the SEM observations of needles growing out of the P3MeT network (Figure 1).

No needles were observed in the deposit when it was stored in the dark, even after 90 days. On the other hand, rapid and abundant needle growth was observed when the deposit was exposed to a stronger white-light irradiation (1300 lx, 7 days): The size of the needles was almost the same as those in Figure 1c. Such rapid growth was also observed from the deposit upon irradiation (1300 lx, 7 days) after 90 days storage in the dark. In addition, immediately after the deposition, a deposit was transferred onto a carbon adhesive tape and exposed to the strong white-light irradiation: after 18 days, no needles were found. All of these observations are consistent with the photo-induced formation of needles in the solid state.

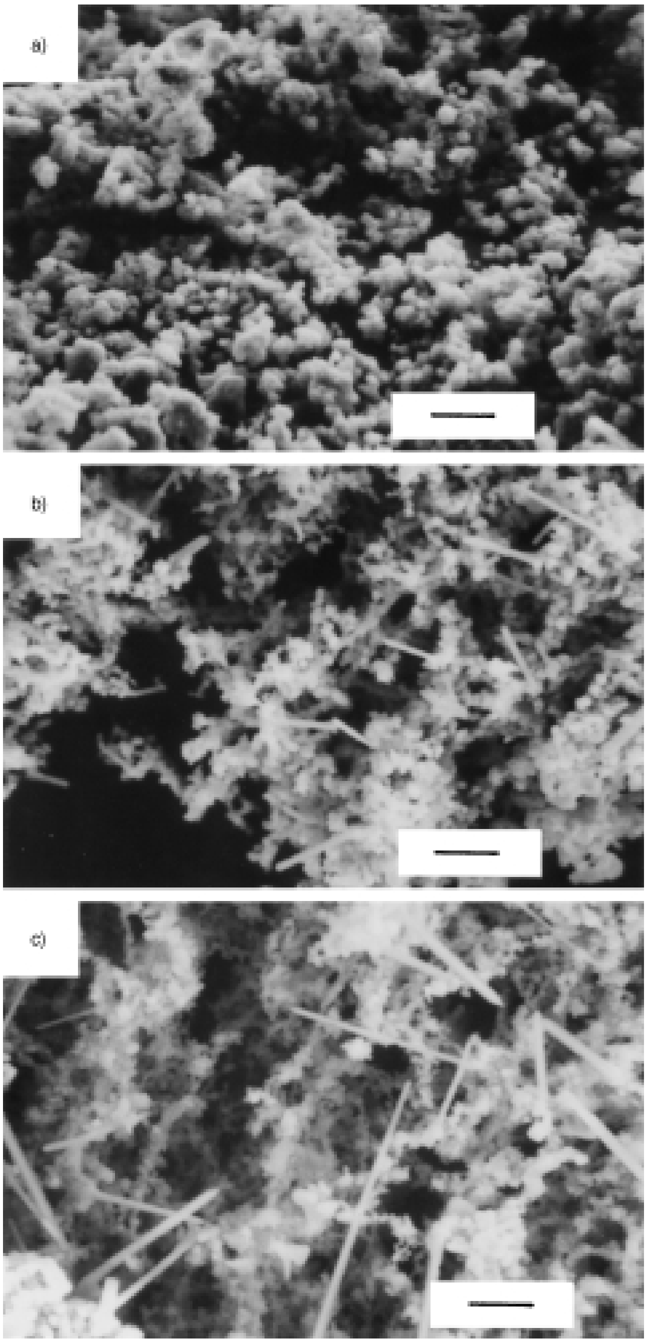

Figure 1. SEM images of the P3MeT deposit on the ETO plate show the evolution and growth of cylindrical needles with white-light irradiation under an ambient atmosphere. Images are taken after a) no exposure, b) 7 days, and c) 45 days. Irregular-shaped conglomerates are the P3MeT deposits. Note that the needles are growing off the deposits. During illumination, the deposits were allowed to stand in contact with the oxide layer. Scale bars: 10 μm.

The following experimental results indicate that the cationic (ammonium) component of the needles is photochemically synthesized from atmospheric dinitrogen. The P3MeT/ETO composite was subject to white-light irradiation (1300 lx, 7 days) in the "closed system" under atmospheres of moist argon and moist nitrogen, to result in no formation and the abundant, rapid growth of needles, respectively. The presence of large amounts of long needles in the latter P3MeT deposit is particularly intriguing: The aspect ratios of some needles were beyond ~1000:1 (Figure 2). The surface of the deposit formed under argon formed no precipitate upon treatment with Nessler's reagent whereas the other formed a brick-red precipitate under the same process and thereby clearly presents evidence of N_2 fixation. X-ray photoelectron spectroscopic analyses (XPS) of a P3MeT specimen, which was prepared on the ETO and then stored in the dark (needle-free sample; Figure 3a), exhibited negligibly small signals at binding energies around $E_b = 400$ eV (N 1s), while two peaks at $E_b = 402.3$ (major) and ~399 eV (minor) were clearly exhibited by a needle-rich sample illuminated (1300 lx) for 7 days (Figure 3b). When combined with the results of the FTIR measurements, the major and minor peaks can be assigned to NH_4^+ and NH_3, respectively.[8] If this is the case, NH_3 is photosynthesized in the composite system and may be converted into NH_4^+. However, the assignment of the signal at ~399 eV is questionable, since it was reported that dinitrogen was oxidized to nitrogen oxide on a TiO_2 surface and that the XPS signal at $E_b = 399.5$ eV might originate from adsorbed nitric oxide or a diatomic nitrogen species.[9] In addition, Figure 3a implies that the P3MeT deposit is only slightly contaminated with environmental NH_3[10] and the TBA^+ ion, which was used as a supporting electrolyte cation. This Figure also indicates that the NH_4^+ does not come from chemical and/or photochemical reactions of such contamination species.

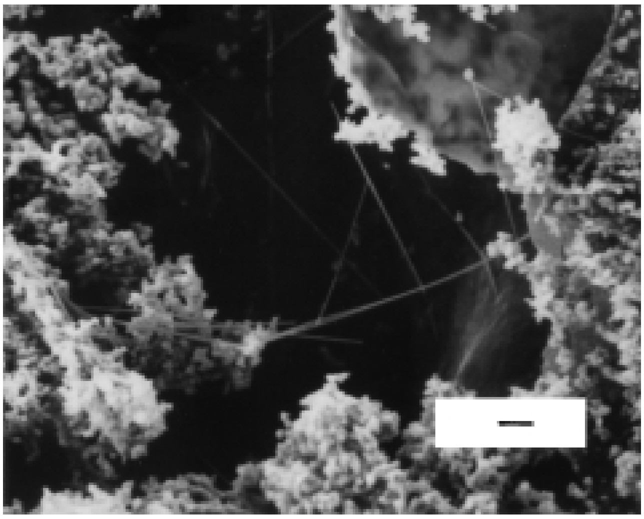

Figure 2. SEM image of a P3MeT deposit exposed to white-light irradiation (1300 lx, 7 days) under a moist N_2 atmosphere. The $NH_4^+ClO_4^-$ needles with high aspect ratios are observed. The bright conglomerates are the edges of the P3MeT deposit. The dark background is the carbon adhesive tape on which the deposit is mounted. Scale bar: 10 µm.

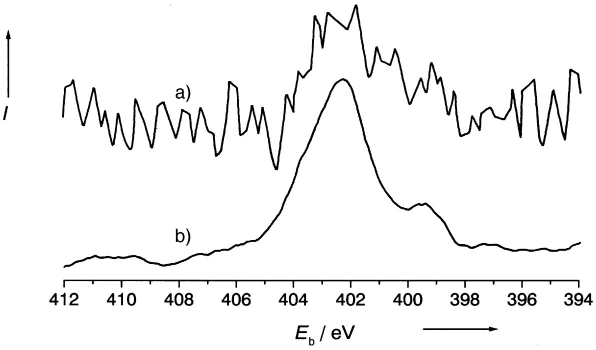

Figure 3. XPS spectra in the nitrogen 1s region for the P3MeT deposit a) stored for 7 days in the dark and b) exposed for 7 days to white-light irradiation (1300 lx). Spectrum (a) was taken under highly sensitive conditions. I = intensity; E_b = binding energy.

The elucidation of the detailed mechanism for needle formation or N_2 fixation awaits further research but these data lead us to speculate on the basic mechanism. Needle formation is initiated by light absorption. Photogenerated carriers at the ETO/P3MeT interface contribute to the synthesis of NH_3 [Eq. (1)] in the presence of adsorbed water according to the finding of Schrauzer and Guth,[1] In parallel with this reaction, ClO_4^--dedoping of P3MeT [Eq. (2)] and proton formation[11] may be induced by the action of photogenerated electrons and holes, respectively, leading to the formation of $HClO_4$. These are most likely followed by an acid-base reaction [Eq. (3)] to form $NH_4^+ClO_4^-$ needles.

$$2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2 \tag{1}$$

$$\mathrm{P3MeT}^{m+}(\mathrm{ClO_4}^-)_m + n\mathrm{e}^- \rightarrow \mathrm{P3MeT}^{(m-n)+}(\mathrm{ClO_4}^-)_{m-n} + n\mathrm{ClO_4}^- \tag{2}$$

$$NH_3 + HClO_4 \rightarrow NH_4^+ClO_4^- \tag{3}$$

How the ammonia synthesis at the interface leads to the needle formation on the free surface of P3MeT, how H^+ is (photo)chemically formed, and what enables the growth of $NH_4^+ClO_4^-$ as needles remain open questions. However, it has been clearly demonstrated that dinitrogen is fixed to a solid ammonium salt using our titanium oxide/conducting polymer system. In view of the fact that the common method of industrial dinitrogen fixation to gaseous ammonia, the Haber process,[12] requires high pressure and temperature, it seems likely that production of solid nitrogen compounds under the mild conditions of our system could become an important process.

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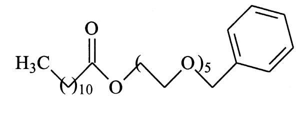
Fatty Acid-Oligo(ethylene glycol) Ester Forms Ion Channels in Lipid Membranes[**]

Tanja Renkes, Hans J. Schäfer,[*] Peter M. Siemens, and Eberhard Neumann[*]

In memory of Eberhard Steckhan

Alkali and alkaline-earth ions can be selectively transported through biological cell membranes by proteins which form ion channels. The passage of ions through these channels can be controlled either by an electrical potential difference or by transmitter molecules.[1, 2] In spite of extensive knowledge on the biophysics of ion conductivity across membranes, the detailed mechanism of transport on the molecular level is still not clear.[2, 3] Since there is only limited access to chemical structures of natural ion channels, either through X-ray structure analysis or NMR spectroscopy,[4] one may identify structural elements by the synthesis and characterization of artificial ion-channel forming compounds.[5] Besides models with peptides as the main structural element, different nonpeptidic structures have been described as ion-channel forming compounds.[6, 7] Of special interest in this connection is **1**, prepared by Menger.[8] Compound **1** is reported to form proton channels by spanning, in a stretched form, the whole length of the lipid membrane. The spontaneous incorporation of **1** in lipid membranes is caused by both the hydrophobic section of the fatty acid chain and by the cationic π-interaction of the benzyl group with the choline group of the lipid. When embedded in the membrane, the oligo(ethylene glycol) chain can cause a localized increase in hydrophilicity of the membrane.[9]



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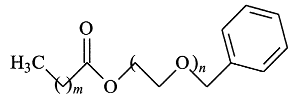
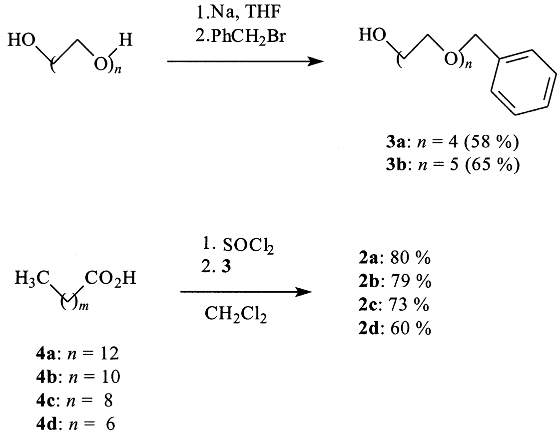
Here, we report the synthesis and characterization of the channel forming compounds **2a**–**d**, which are structurally similar to **1** but vary in the length of the fatty acid and the oligo(ethylene glycol). The activity of the channels has been analysed by fluorescence spectroscopy and, for the first time, by the electrical conductivity of single channels.



2a: $m = 12$, $n = 4$
2b: $m = 10$, $n = 4$
2c: $m = 8$, $n = 5$
2d: $m = 6$, $n = 5$

The channel-forming compounds **2a**–**d** are obtained in two steps. First, tetra- and pentaethylene glycol are converted by a Williamson ether synthesis into the corresponding monobenzyl ether **3a** and **3b**. These are then esterified with fatty acids **4a**–**d** to form **2a**–**d** (Scheme 1).



Scheme 1. Preparation of the channel-forming compounds **2a**–**d**.

In order to examine their activity as channel-forming compounds the esters **2a**–**d**, compound **1** and gramicidin D were integrated into lipid vesicles consisting of 1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholin (DPPC). The rate of the ionic flux through the vesicle membrane was determined by time-resolved fluorescence spectroscopy, in which pyranine served as a pH indicator. When excited at 450 nm, pyranine exhibits a maximum in the emission spectrum at 511 nm for pH values above 7.2; this intensity maximum strongly decreases at pH values below 7.2.[10] The DPPC vesicles were prepared and suspended in a weakly buffered pyranine solution (pH 7.7).[11] Pyranine outside the vesicles was then removed by two passes through a gel filtration unit, such that the fluorescence of the probe is exclusively due to the pyranine inside the vesicles and it can therefore be used as a measure of the proton concentration. Decreasing the pH value

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[*] Prof. Dr. H. J. Schäfer, Dipl.-Chem. T. Renkes
Institut für Organische Chemie der Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-8339772
E-mail: schafeh@uni-muenster.de

Prof. Dr. E. Neumann, Dipl.-Chem. P. M. Siemens
Physikalische und Biophysikalische Chemie
Fakultät für Chemie
Universität Bielefeld
Postfach 10 01 31, 33501 Bielefeld (Germany)
Fax: (+49) 521-1062981
E-mail: eberhard.neumann@uni-bielefeld.de

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