Electron/Ion-Conducting Materials

Towards the Development of Electrical Conduction and Lithium-Ion Transport in a Tetragonal Porphyrin Wire**

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Dedicated to Professor Yu Wang
on the occasion of her 60th birthday

The development of porous organic solids that can simultaneously support the transport of both electrons and lithium ions is of considerable technological importance for several fields of research, such as solid-state lithium batteries, nanoelectronics, and nanotechnologies.[1–6] Towards this goal, the following requirements should be satisfied: 1) construction of a robust open framework, 2) introduction of good conductivity, and 3) use of lithium motion channels. One can learn by studying naturally occurring membranes, such as the thylakoid membrane in a chloroplast envelope,[7] in which channels or pores control ion flow, charge transport, and signal transduction. Hence, self-assembly of π-conjugating supramolecules may be a powerful tool in the production of suitable functional materials.[8–10] Metallophthalocyanine stacks have been intensively studied as organic conductors,[11] but related porphyrins have attracted less attention. Although a large number of porphyrin-based supramolecules have been synthesized,[12–14] the discotic phase self-assembly of porphyrins is difficult to perform in a controlled manner. Herein, we report the design of a hybrid electronic/ionic conduction material based on a self-assembled porphyrin architecture in which tetragonal packing gives rise to square iodine-channels and prophyrin wires.

During the exploration of new classes of π-functional coordination zeolites under hydrothermal techniques,[15] one-step C–N$^+$(sp^2) bond formation was found serendipitously, thereby opening the way to the rational design and synthesis of 1D porphyrin wires. Solvothermal reactions of H_2TPyP (H_2TPyP = 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine), CdI_2, I_2, CH_3CH_2OH, and CH_3COOH in the molar ratio 1:2:10:680:700 at 180 °C for 72 h produced purple crystals. The solvothermal synthesis is reproducible and gives the product in high yield (87 %). The X-ray structural analysis of these purple crystals (Figure 1) reveals an infinite wirelike chain, $[H_2TPyPR_4]_n^{4+}$. (**1**; R = CH_2CH_3), in which the porphyrin molecules assemble into columnar aggregates sustained by cooperative π-facial hydrogen bonds. The dihedral angle formed between the plane of the pyridine ring and that of the porphyrin is around 96°. The interatomic CH···π and H···π distances of 2.99 Å and 2.33 Å, respectively, are indicative of π-facial hydrogen bonding (i.e., less than 2.6 Å). As polycationic backbones are created, the charge-compensating tetrahedral CdI_4^{2-} ions are self-included, which stabilizes the prophyrin wires through CH···I hydrogen bonds, aromatic π···I, and N$^+$···I (4.0 Å) electrostatic interactions. The cylindrical prophyrin wires are further glued together by a combination of efficient van der Waals (vdW) and electrostatic interactions, thus yielding tetragonal packing rather than hexagonal topologies (Figure 1 b). Therefore, the secon-

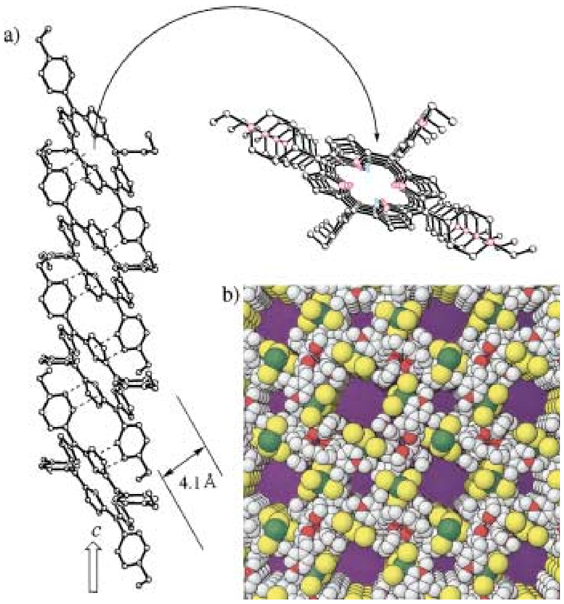

Figure 1. Molecular structure of **1**. a) Ball-and-stick representation of self-assembling prophyrin wires from porphyrins through CH···π interactions (-----). b) Space-filling view of the open-framework structure of **1** along the crystallographic *c* axis. If the van der Waals radius of an iodine ion (2.1 Å) is taken into account, the square iodine channels have the dimension of 6×6 Å^2. Hydrogen and solvent molecules are omitted for clarity. (C: white; N: red; Cd: green; I: yellow).

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dary building unit was identified with the general formula $[(H_2TPyPR_4)(CdI_4)_2]_4 \cdot G$ (G = guest molecules, determined to be $8\,H_2O$ and $4\,CH_3COOH$ per unit cell).

The benefits of the presence of two types of functional channel, namely the iodine channels and prophyrin wires in **1,** have prompted us to study the development of the hybrid transport of electrons and lithium ions, the strategy of which is given in Figure 2. The most intriguing feature of **1** is the presence of the highly disordered guest molecules trapped in the square pores. The stability of the framework was assessed by thermogravimeteric analysis (TGA) and powder X-ray-diffraction (XRD) studies. TGA reveals that the guest molecules were released below 100 °C, whereas no weight loss was observed between 100 and 350 °C. When the sample was heated at 250 °C for 8 h, the powder XRD patterns remained unchanged relative to the unheated sample of **1**, which indicates that the porous framework was retained even after the loss of some solvent molecules. Therefore, the structure is robust enough to sustain such open spaces in the crystal caused by the loss of guest molecules. Given the thermal and structural stability of the open framework, we aspired to create nanostructures that are electrical conductors by intercalation methods. With a bottom-up nanoelectronic approach in mind, we examined the encapsulation of conducting polyaniline (PANI) molecules in the 1D iodine channels (Figure 2, I). The adsorption–desorption behavior of aniline molecules was studied between 40–150 °C; the TGA traces for cooling and heating scans are given in Figure 3 a. These traces reveal a reversible aniline sorption in the pores of **1**. Furthermore, the electronic reflectance spectrum of PANI@**1** reveals an additional peak at 468 nm, which is attributed to emeraldine polyaniline (Figure 3 b).[16] Consequently, the conductivity of PANI@**1** is approximately 10^{-3} S cm^{-1}, which is an increase of six orders of magnitude compared to that of **1** (10^{-9} S cm^{-1}; Figure 3 c). This result demonstrates that the conjugated polymers can be encapsulated in the nanoscale channels and still support mobile charge carriers.

Another unusual feature of **1** is that the porphyrin wires may function as a transport matrix for lithium ions by ion-exchange processes (Figure 2, II). The feasibility of the lithium-ion insertion was investigated by using a C/Li·PANI@**1** cell, which involves simultaneous intercalation–deintercalation of lithium ions in two-electrode host materials. Some preliminary reversible cycling data are presented in Figure 4. The cyclability of the cell was determined to be over 100 cycles between 0 and 2 V, which indicates that lithium

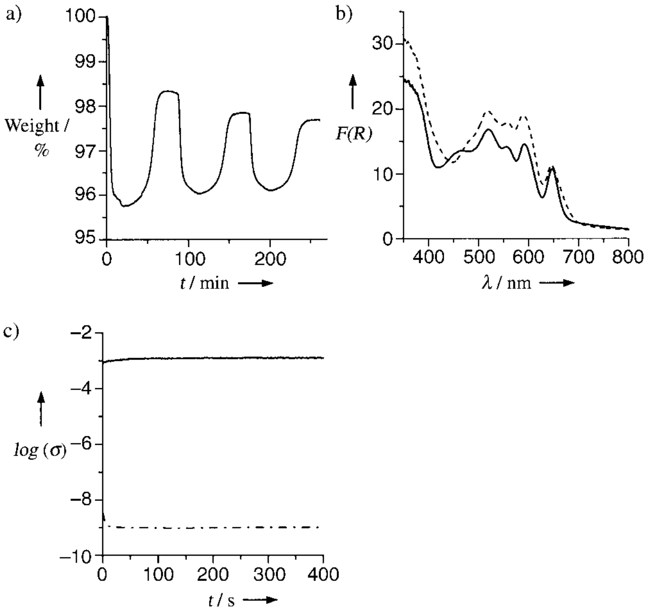

Figure 3. a) TGA profile of the reversible adsorption-desorption of aniline on **1**. Repeated heating and cooling cycles were conducted between 40–150 °C. b) Diffuse reflectance spectra of **1** (-----) and PANI@**1** (——), showing one envelope of the feature at about 468 nm, which is attributed to PANI in addition to four visible Q bands from the porphyrin at 517, 558, 589, and 646 nm. The relative reflectance for a powder, $F(R)$, is given by $F(R) = (1-R)^2/2R$, where R is the ratio of reflected intensity of the sample to that of a nonabsorbing standard. c) Electrical conductivity (σ/S cm^{-1}) of **1** (–•–•) and PANI@**1** (——).

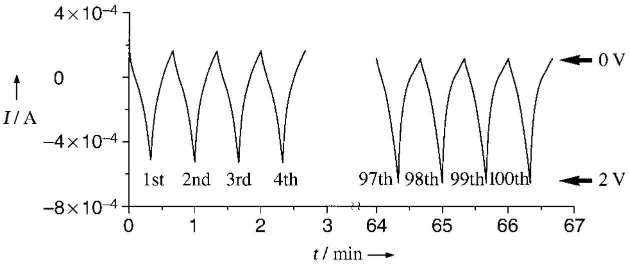

Figure 4. Cyclic voltammogram of a C/Li·PANI@**1** cell. A 1 M solution of $LiClO_4$ in EC–DMC–MF was used as the electrolyte (T = 30 °C, scan rate 100 mV s^{-1}). Measurements between 0 and 2 V revealed the cyclability of Li·PANI@**1** by intercalating/de-intercalating lithium ions. I = current.

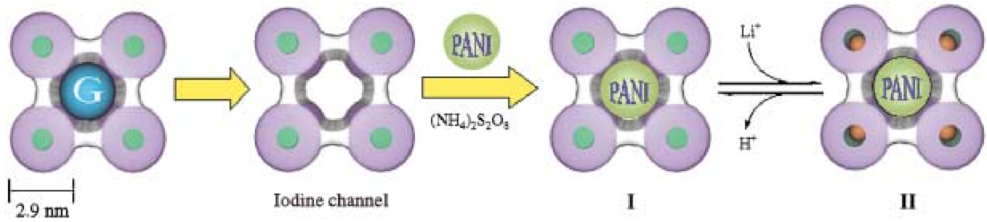

Figure 2. Scheme showing two routes to the development of electrical conductivity for **1**: I: the encapsulation of conducting polyaniline (PANI) into iodine cavities; II: the insertion of a lithium ion into the prophyrin wires through proton–lithium ion-exchange processes.

ions and electrons can be removed and reinserted in **1**; such cyclability is a key aspect of lithium batteries.[17] An intriguing question is whether lithium ions intercalate in porphyrin wires. Using electron reflectance spectroscopy as the diagnostic technique, we found that the chromophore of the porphyrin was perturbed with significant changes in the visible Q band (i.e. a red shift of 27 nm),[18] because metal-ion insertion leads to an increase in the electron density of the porphyrin wire. This result has encouraged us to focus on optimizing the intercalation and obtaining a precise understanding of the lithium-ion-insertion mechanism.

In summary, we have demonstrated the first porous organic solids capable of mediating hybrid electronic/ionic conduction. This work may lead to the development of lithium-battery materials and a new lithium-sensitive electrode for the determination of the concentration of lithium ions in body fluids.

Experimental Section

Synthesis of **1**: A mixture of H_2TPyP (0.0732 g), CdI_2 (0.0619 g), I_2 (0.3 g), CsOH (0.3 mL), CH_3COOH (4 mL), and ethanol (4 mL) was sealed in a 23 mL Telflon-lined stainless-steel autoclave and heated to 180 °C for 48 h, then cooled to 70 °C at a rate of $6\,K\,h^{-1}$. Purple needles (0.1847 g, 87 % based on H_2TpyP) were isolated by filtration from the reaction mixture, and washed with ethanol. This synthesis was highly reproducible. X-ray data: tetragonal, space group $P4_2/n$, $a = b = 29.078(3)$, $c = 8.134(1)$ Å, $V = 6872(1)$ Å^3, $R_1 = 0.065$, $wR_2(F^2) = 0.173$, GOF = 0.943. The pore solvent molecules could not be completely located in the structure analysis. Furthermore, a preliminary N_2 adsorption/desorption isothermal study indicated that the pore size is around 5.6 Å. CCDC-158530 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Fitting the formula composition with the elemental analysis, and thermogravimetric analysis (weight loss of 4.3 %), we found a composition that contains four acetic acid molecules and eight water molecules per unit cell in these channels. (Elemental analysis (%): calcd: C 29.00, N 5.41, O 3.09, H 2.63; found: C 28.21, N 5.42, O 3.40, H 2.92).

Inclusion of polyaniline filaments in **1**: The structure of **1** has an open pore size of about 0.6 nm in diameter. The molecule-size channels of these hosts limit the thickness of polymer filaments to molecular dimensions. Aniline vapor was diffused into the desolvated **1** at 60 °C for 24 h. The resulting product was isolated by filtration and washed thoroughly with $CHCl_3$ to remove aniline molecules on the solid surface of **1**. The presence of aniline in **1** was determined by ^1H NMR spectroscopy (600 MHz, $\delta = 7.002$, 7.088, and 7.173 ppm). The aniline@**1** product was suspended in ethanol (25 mL), and a solution of peroxydisulfate was added. The suspension was stirred at 0 °C for 4 h and the purple-green solid was isolated by filtration, washed with ethanol and dried at 60 °C.

Cyclic voltammogram of a C/Li·PANI@**1** cell: Owing to the robust nature of the host of **1**, the prophyrin wires have a strong affinity for lithium insertion or ion-exchange. Li·PANI@**1** solids were obtained after immersion of the PANI@**1** solids in a solution containing Lithium ions. The presence of Li^+ in PANI@**1** was determined by ^7Li NMR spectroscopy, as a signal was observed at $\delta = -1.735$ ppm relative to that of free $LiNO_3$. Furthermore, the cathode was fabricated by compressing powdered Li·PANI@**1** (85 %), black carbon (10 %), and PTFE (5 %) on to an aluminum disk. The pellet was then dried at 120 °C in air. The electrolyte was prepared by dissolving $LiClO_4$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and methyl formate (MF) (volume ratio 50:45:5) to give a 1 M solution. Some properties of the cathode and of the electrolyte were reported.[19]

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[1] J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359 – 367.
[2] Z. Gadjourova, Y. G. Andreev, D. P. Tunstall, P. G. Bruce, *Nature* **2001**, *412*, 520 – 523.
[3] T. Nakamura, T. Akutagawa, K. Honda, A. E. Underhill, A. T. Coomber, R. H. Friend, *Nature* **1998**, *394*, 159 – 162.
[4] R. F. Service, *Science* **2002**, *295*, 2398 – 2399.
[5] L. W. Huang, C. J. Yang, K. J. Lin, *Chem. Eur. J.* **2002**, *8*, 396 – 400.
[6] J. R. Dahn, T. Zheng, Y. Liu, J. S. Xue, *Science* **1995**, *270*, 590 – 593.
[7] D. O. Hall, K. F. Rao, *Photosynthesis, 4th ed*, Cambridge University, Cambridge, **1988**, p. 98.
[8] M. R. Ghadiri, J. R. Granja, L. K. Buehler, *Nature* **1994**, *369*, 301 – 304.
[9] O. Ikkala, G. T. Brinke, *Science* **2002**, *295*, 2407 – 2409.
[10] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119 – 1122.
[11] a) T. Inabe, J. G. Gaudiello, M. K. Moguel, J. W. Lyding, R. L. Burton, W. J. McCarthy, C. R. Kannewurf, T. J. Marks, *J. Am. Chem. Soc.* **1986**, *108*, 7595 – 7608, and references therein; b) J. Ern, A. Bock, L. Oddos-Marcel, H. Rengel, G. Wegner, H. P. Trommsdorf, C. Kryschi, *J. Phys. Chem. A* **1999**, *103*, 2446 – 2450; c) R. Silerva(Back), L. Kalvoda, D. Neher, A. Ferencz, J. Wu, G. Wegner, *Chem. Mater.* **1998**, *10*, 2284 – 2292; d) C. W. Dirk, T. Inabe, K. F. Schoch, Jr., T. J. Marks, *J. Am. Chem. Soc.* **1983**, *105*, 1539 – 1550; e) H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 972 – 981.
[12] a) Y. Diskin-Posner, S. Dahal, I. Goldberg, *Angew. Chem.* **2000**, *112*, 1344 – 1348; *Angew. Chem. Int. Ed.* **2000**, *39*, 1288 – 1292, and reference therein; b) B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, *369*, 727 – 729; c) S. Belanger, J. T. Hupp, *Angew. Chem.* **1999**, *111*, 2360 – 2362; *Angew. Chem. Int. Ed.* **1999**, *38*, 2222 – 2224; d) C. M. Drain, F. Nifiatis, A. Vasenko, J. D. Batteas, *Angew. Chem.* **1998**, *110*, 2478 – 2481; *Angew. Chem. Int. Ed.* **1998**, *37*, 2344 – 2347; e) T. Schareina, R. Kempe, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1279 – 1281; f) K.-J. Lin, *Angew. Chem.* **1999**, *111*, 2894 – 2897; *Angew. Chem. Int. Ed.* **1999**, *38*, 2730 – 2732; g) M. E. Kosal, J. H. Chou, S. Wilson, K. S Suslick, *Nature Mater.* **2002**, *1*, 118 – 121.
[13] M. P. Byrn, C. J. Curtis, I. Goldberg, Y. Hsiou, S. I. Khan, P. A. Sawin, S. K. Tendick, C. E. Strouse, *J. Am. Chem. Soc.* **1991**, *113*, 6549 – 6557.
[14] C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger, R. D. Rogers, *J. Am. Chem. Soc.* **1999**, *121*, 1137 – 1144.
[15] S. F. Lia, C. Y. Cheng, K. J. Lin, *Chem. Commun.* **2001**, 1082 – 1083.
[16] a) P. Enzel, T. Bein, *J. Phys. Chem.* **1989**, *93*, 6270 – 6272; b) C. G. Wu, T. Bein, *Science* **1994**, *264*, 1757 – 1759.

[17] The current density of PANI dramatically decreased as the cycling number increased because of the lack of Li^+ storage ability in PANI, while the redox electroactivity of Li·PANI@**1** was over 200 cycles. Thus, a new approach to the development of a composite organic lithium-battery material was achieved in the presence of PANI in **1**. This result will be reported later.

[18] It reveals a red shift of the Q band by 9 nm for Fe^{2+}, but no influence for Na^+ and K^+. This result illustrates that the ion exchange takes place when the diameters of metal ions (Li^+ 1.48 Å; Na^+ 2.04 Å) are smaller than that of the porphyrin core (1.56 Å).

[19] a) A. R. Armstrong, P. G. Bruce, *Nature* **1996**, *381*, 499–500; b) S. R. S. P. Prabaharan, M. S. Michael, S. Radhakrishna, C. Julien, *J. Mater. Chem.* **1997**, *7*, 1791–1796.