was then removed by high vacuum and a chloroform solution of polymer PmPV′ was added (5 mg in 5 mL). Sonication for 2 h gave a stable suspension that was filtered prior to spectroscopy.

Preparation of the SWNT/PmPV′ material prior to AFM: Aliquots of Triton X-100 SWNTs (from Tubes@Rice) were purified by centrifugation at 14000 rpm in MeOH. The purified tubes were re-suspended in fresh MeOH by shaking, and then they were vacuum filtered over a 0.2 mm PTFE filter and washed with MeOH and 18 MQ H_2O to form a nanotube mat. A portion of the mat weighing 6–7 mg was sonicated in DMF using a bath sonicator while stepwise adding the DMF until a total volume of 25 mL was obtained. The DMF/NT stock solution was sonicated for a period of 6 h. Measured aliquots of the stock solution were transferred to round-bottom flasks and the DMF was removed by rotary evaporation. Each flask contained between 0.24–0.32 mg of SWNTs. 5 mL of $CHCl_3$ containing between 0.2–1.0 mg of dissolved PmPV were added to these flasks. The SWNT/PmPV′ mixtures were sonicated for 15 mins. After sonication, one drop of the SWNT/PmPV′ solution was placed on a freshly cleaved 1 cm^2 mica wafer, and subsequently washed with 5 drops of $CHCl_3$ while spinning it at 750 rpm to wash off the excess of the polymer. AFM images were collected in noncontact mode.

Received: December 18, 2000 [Z16297]

[1] S. Ijima, T. Ichihashi, *Nature* **1993**, *363*, 603–605.

[2] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787–1799.

[3] a) S. J. Tans, C. Dekker, *Nature* **2000**, *404*, 834–835; b) S. J. Tans, A. R. M. Verschueren, C. Dekker, *Nature* **1998**, *393*, 49–52; c) S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, C. Dekker, *Nature* **1997**, *386*, 474–477.

[4] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622–625.

[5] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253–1256.

[6] a) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95–98; b) M. A. Hamon, J. Chen, H. Hu, Y. Chen, M. E. Itkis, A. M. Rao, P. C. Eklund, R. C. Haddon, *Adv. Mater.* **1999**, *11*, 834–840; c) J. E. Riggs, Z. Guo, D. L. Carroll, Y.-P. Sun, *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.

[7] a) E. T. Mickelson, C. B. Huffman, A. G. Rinzler, R. E. Smalley, R. H. Hauge, J. L. Margave, *Chem. Phys. Lett.* **1998**, *296*, 188–194; b) E. T. Mickelson, I. W. Chiang, J. L. Zimmerman, P. J. Boul, J. Lozano, J. Liu, R. E. Smalley, R. H. Hauge, J. L. Margrave, *J. Phys. Chem. B* **1999**, *103*, 4318–4322; c) P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *310*, 367–372.

[8] Polymers that have been used to prepare composites with SWNTs include polymethylmethacrylate, see: a) M. Yudasaka, M. Zhang, C. Jabs, S. Ijima, *Appl. Phys. A* **2000**, *71*, 449–451; b) C. Stephan, T. P. Nguyen, M. Lamy de la Chapelle, S. Lefrant, C. Journet, P. Bernier, *Synth. Met.* **2000**, *108*, 139–149. Polymers have also been used to prepare composites with multi-walled nanotubes, see: c) M. S. P. Shaffer, A. H. Windle, *Adv. Mater.* **1999**, *11*, 937–941; d) Z. Jin, X. Sun, G. Xu, S. H. Goh, W. Ji, *Chem. Phys. Lett.* **2000**, *318*, 505–510. Recently, polymers have been used in the spinning of SWNTs into long fibers, see: e) B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, P. Poulin, *Science* **2000**, *290*, 1331–1334.

[9] a) S. A. Curran, P. M. Ajayan, W. J. Blau, D. L. Carroll, J. N. Coleman, A. B. Dalton, A. P. Davey, A. Drury, B. McCarthy, S. Maier, A. Strevens, *Adv. Mater.* **1998**, *10*, 1091–1093; b) S. Curran, A. P. Davey, J. N. Coleman, A. B. Dalton, B. McCarthy, S. Maier, A. Drury, D. Gray, M. Brennan, K. Ryder, M. Lamy de la Chapelle, C. Journet, P. Bernier, H. J. Byrne, D. Carroll, P. M. Ajayan, S. Lefrant, W. Blau, *Synth. Met.* **1999**, *103*, 2559–2562; c) J. N. Coleman, A. B. Dalton, S. Curran, A. Rubio, A. P. Davey, A. Drury, B. McCarthy, B. Lahr, P. M. Ajayan, S. Roth, R. C. Barklie, W. J. Blau, *Adv. Mater.* **2000**, *12*, 213–216.

[10] a) A. P. Davey, A. Drury, S. Maier, H. J. Byrne, W. J. Blau, *Synth. Met.* **1999**, *103*, 2478–2479; b) O. Toshihiro, N. Takanobu, D. Shuji (Sumitomo Chemical Co), EP0901174, **1999** [*Chem. Abstr.* **1999**, *139*, 202731c]; c) Y. Pang, J. Li, B. Hu, F. E. Karasz, *Macromolecules* **1999**, *32*, 3946–3950.

[11] Computer modeling (molecular mechanics and molecular dynamics simulations) has been carried out by us to probe the nature of the interaction between a short (10,10)-SWNT and a PmPV′ of eight repeating units. These calculations support a model in which the polymer is wrapped helically around the nanotubes with the phenylene rings in the polymer backbone stacked in a "face-to-face" manner against the walls of the nanotube. For another recent example of calculations carried on the binding of different polymers to carbon nanotubes, see V. Lordi, N. Yao, *J. Mater. Res.* **2000**, *15*, 2770–2779.

[12] For an early report on polymeric light-emitting diodes (LEDs) based on poly(paraphenylenevinylene) (PPV), see J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K, Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539–541.

[13] For an excellent review on electroluminescent conjugated polymers, see A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416–443; *Angew. Chem. Int. Ed.* **1998**, *37*, 402–428.

[14] S. Henrichs, J. Sample, J. Shiang, C. P. Collier, R. J. Saykally, J. R. Heath, *J. Phys. Chem. B* **1999**, *103*, 3524–3528.

T_h-Symmetric Nanoporous Network Built of Hexameric Metallamacrocycles with Disparate Cavities for Guest Inclusion**

Cheng-Yong Su, Xiao-Ping Yang, Bei-Sheng Kang,* and Thomas C. W. Mak*

Growing interest in the rational design and construction of nanoporous structures[1] is motivated principally by the potential exploitation of the resulting cavities and channels in nanotechnology, including shape- and size-selective catalysis, molecular recognition, ion exchange, separation, and optoelectronic applications.[2] Rapid growth and breakthroughs in this field rely on, to a large degree, mastery of the novel synthetic protocol in the construction of organized supramolecular systems, namely self-assembly of multiple building blocks in a single step into large aggregates of molecules through noncovalent interactions.[3] On the other hand, difficulties were often encountered in the generation of porous networks, such as the control of cavity size and geometry, the prevention of network interpenetration, and

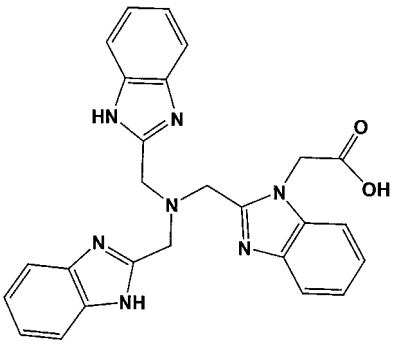
[*] Prof. B.-S. Kang, Dr. C.-Y. Su, X.-P. Yang
School of Chemistry and Chemical Engineering
Zhongshan University
Guangzhou 510275 (PR China)
Fax: (+86) 20-84110318
E-mail: cesscy@zsu.edu.cn
Prof. T. C. W. Mak
Department of Chemistry
The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong SAR (PR China)
Fax: (+852) 26035057
E-mail: tcwmak@cuhk.edu.hk

[**] This work is supported by the National Natural Science Foundation of China, the Natural Science Foundation of Guangdong Province and Hong Kong Research Grants Council Earmarked Grant CUHK 4206/99P.

the irreversible collapse of an open network upon the removal of absorbates.[1a, 4]

Recent advances in molecular architecture[5–7] have pointed the way to a promising strategy for overcoming these drawbacks. For instance, noninterpenetrating networks may be formed by using large molecular aggregates as secondary building blocks. In an earlier study, $[\{M(CO)_3(\mu_3\text{-}OH)\}_4]$ (M = Mn, Re) clusters were used to assemble super-diamondoid networks to a lower level of interpenetration.[8] More recently, large inorganic clusters have been exploited to generate open, noninterpenetrating networks of nanoscale porosity.[9, 10]

Our investigation of metal complexes with tripodal ligands has revealed that C_3-symmetric tris(2-benzimidazolylmethyl)-amine (ntb) can encapsulate lanthanide(III) and silver(I) ions to afford large hexafunctional hydrogen-donor building blocks,[11] which were further assembled to form doubly interpenetrating three-dimensional (3D) stereoisomeric networks[11a] or rhombohedral networks with large cavities.[11b] These findings prompted us to utilize even larger molecular aggregates as subunits to fabricate nanoporous networks. To achieve this goal, we employed the branched unsymmetric tripodal ligand *N*-[*N*′-(carboxymethyl)benzimidazol-2-ylmethyl]-*N*,*N*-bis(benzimidazol-2-ylmethyl)amine (HAcntb),



HAcntb

which was derived from ntb by attachment of one acetic acid group. Reaction of its sodium salt Na(Acntb) with an equal molar amount of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol afforded $[Cu_6(Acntb)_6](ClO_4)_6 \cdot nH_2O$ ($\mathbf{1} \cdot 6ClO_4 \cdot nH_2O$), which crystallized as beautiful green octahedra from slow evaporation of the reaction mixture. The elemental analysis results showed that the number of solvated water molecules in the stoichiometric formula of the complex varied according to the condition of crystallization. A freshly prepared sample in aqueous ethanol may incorporate as many as 38 water molecules, while that recrystallized from a nonaqueous solvent medium usually contains less. In any event the IR spectral data indicated that the framework of the complex remains unchanged although the guest molecules may vary, and FAB mass spectrometry confirmed the presence of the $[Cu(Acntb)]^+$ basic unit in all cases.

Crystallographic analysis revealed a nanometer-sized cationic hexanuclear metallamacrocycle $[Cu_6(Acntb)_6]^{6+}$ (**1**); the linkage between two adjacent $[Cu(Acntb)]^+$ components is shown in Figure 1. Each copper(II) ion is coordinated by three

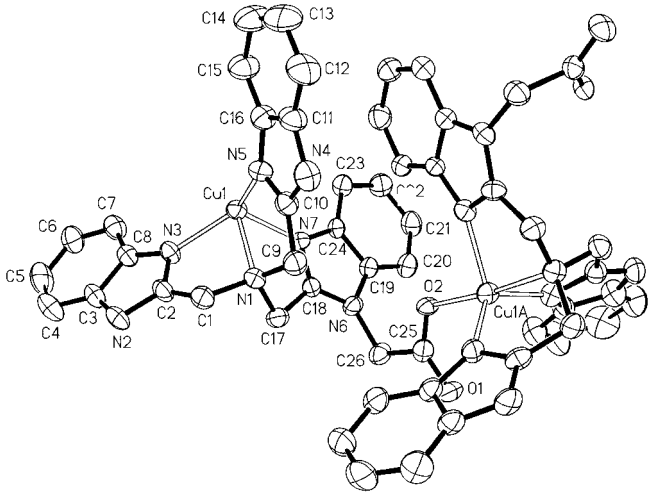


Figure 1. Linkage between two adjacent $[Cu(Acntb)]^+$ units showing the bridging mode of the monodentate $Acntb^-$ ligand and the coordination geometry about a copper(II) ion. The atoms are drawn as thermal ellipsoids at the 30% probability level.

imino-nitrogen atoms and the apical amino-nitrogen atom of an $Acntb^-$ ligand, and the branching acetate group functions as a monodentate bridge between adjacent $[Cu(Acntb)]^+$ units, thus generating a hexameric macrocycle with a crystallographic $\bar{3}$ axis passes through the center of the hexamer. Viewing down the $[1\bar{1}1]$ direction, **1** resembles a nanoscale wheel of diameter 23.3 Å with six fan-blade-like benzimidazole rings (Figure 2). The remaining twelve benzimidazole

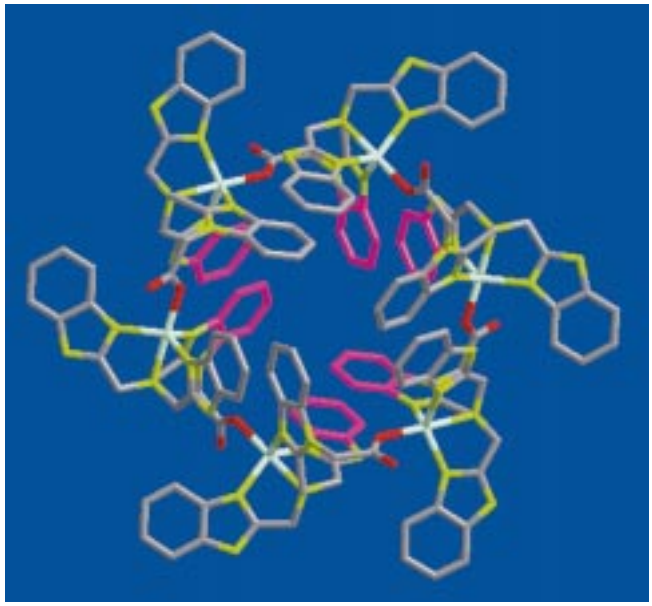


Figure 2. A view of the hexanuclear metallamacrocyclic nano-wheel $[Cu_6(Acntb)_6]^{6+}$ (**1**).

rings wrap inward around the $\bar{3}$ axis, affording a hydrophobic cavity with a smallest diameter of 6 Å. The $[Cu_6(Acntb)_6]^{6+}$ giant wheel has a vaulted core with a thickness of 12 Å, looking somewhat like a "flying saucer" when viewed from the side.

  0044-8249/01/11309-1776 $ 17.50+.50/0

The distinguishing feature of **1** is that it is conformationally rigid, with all six noncoordinated carboxylato oxygen atoms and twelve amino NH groups involved in hydrogen bonding. For each $[Cu_6(Acntb)_6]^{6+}$ molecule, six abducent NH groups belonging to fringe benzimidazole rings form donor bonds with the carboxylato O atoms of six neighboring molecules, while the six carboxylato O atoms are arranged alternately above and below the wheel to form acceptor hydrogen bonds with another six neighbors. Thereby a total of twelve $\bar{3}$ symmetry-related N–H···O hydrogen bonds (N···O 2.840 Å) generate an open, three-dimensional cationic network with T_h symmetry (Figure 3). Huge octahedral voids

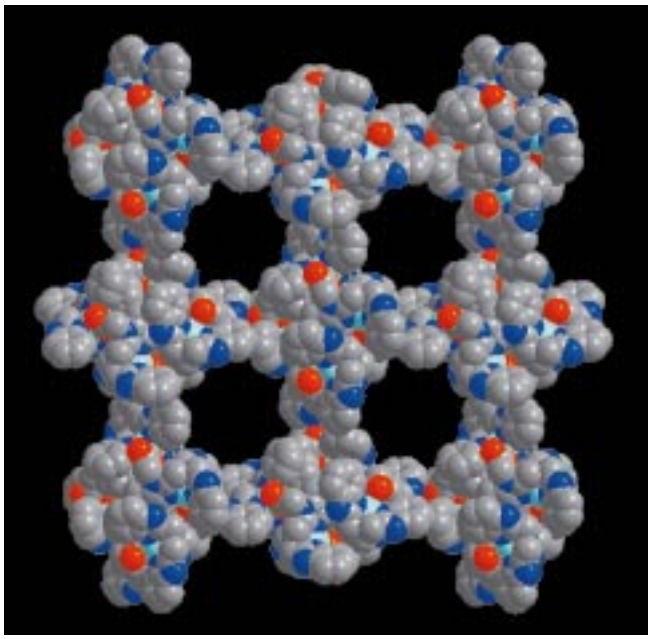


Figure 3. Space-filling diagram of the 3D network viewed along [100]. All guest molecules are omitted for clarity.

with estimated dimensions of $11 \times 11 \times 14$ Å are formed, in which another six NH groups provide a hydrophilic environment to accommodate the guest molecules. In total 26 water molecules and six perchlorate anions are located within each cavity, which has essential windows for inclusion and escape of guest molecules. Calculation using the PLATON program[12] suggests that the effective volume for inclusion is about 8886 Å^3, comprising 42% of the crystal volume. Since the macrocyclic aggregate itself has an empty intramolecular hydrophobic cavity, selective inclusion of different guests by molecular recognition should be possible.

The possibility of exchanging the solvent water molecules in the cavity for other organic molecules of different polarity was also investigated. The IR spectrum of a freshly prepared complex that had been soaked in chloroform for several hours did not show any difference from the original complex, and the elemental analysis suggested that the stoichiometric formula remained unchanged.[13] However, after the complex was recrystallized in acetone/ethanol (1:20), a new stretching carbonyl band appeared at 1697 cm^{-1}, and elemental analysis also indicated inclusion of the acetone molecules.[14] This finding may be attributed to the fact that acetone, being a stronger hydrogen-bond acceptor than chloroform, can easily replace water molecules in the void. Thermogravimetric analysis (TGA) of ($\mathbf{1} \cdot 6ClO_4 \cdot 38H_2O$) showed two continuous weight losses (total about 15%) in the range 26–160 °C, followed by another (about 14%) in the range 200–280 °C, corresponding to respective liberation of solvated water molecules and perchlorate anions. The major weight loss (about 60%) occurred in the range 340–580 °C, which may correspond to complete destruction of the network. This study indicated that the guest water molecules can escape from the cavity even at low temperature. However, the complete liberation of water molecules over an extended range of 134 °C is suggestive of complex interactions between host and guest, or even between different guest molecules.

To the best of our knowledge nanoporous structures assembled with large molecular architectures as building blocks are seldom investigated.[15] The present study provides the first example of a hydrogen-bonding sustained T_h-symmetric, open network constructed from nanosized metallamacrocylic molecules. Precise self-assembly of the hexameric aggregate **1** is facilitated by the branch-functionalized tripodal ligand Acntb$^-$, whose deliberately positioned hydrogen-bond donors and acceptors effectively prevent network interpenetration. The formation of multiple directional hydrogen bonds between the conformationally rigid metallamacrocycles consolidates the 3D network. Another feature that makes this kind of synthetic strategy commendable is the concomitant generation of both intra- and intermolecular host cavities,[16] allowing possible fine-tuning of molecular recognition characteristics and selective enclosure of different guest molecules.

Experimental Section

1: $Cu(ClO_4)_2 \cdot 6H_2O$ (0.019 g, 0.05 mmol) dissolved in EtOH (5 mL) was added to a solution of Na(Acntb) (0.024 g, 0.05 mmol) in EtOH (50 mL). The color turned green rapidly and the resulting mixture was stirred for 2 h. After filtration, the solution was left standing for several days to afford a green crystalline product. IR (KBr): $\tilde{\nu} = 3387, 3061, 1625, 1544, 1498, 1476, 1451, 1385, 1278, 1115, 1085, 747, 626\ cm^{-1}$; FAB-MS: m/z: 528 $[Cu(Acntb)]^+$, 628 $[Cu(Acntb)(ClO_4)]^+$; elemental analysis indicated the stoichiometric formula of $[Cu_6(Acntb)_6](ClO_4)_6 \cdot 38H_2O$, calcd for $C_{156}H_{208}Cl_6N_{42}O_{74}Cu_6$ (%): C 42.11, H 4.71, N 13.22; found: C 42.04, H 5.06, N 13.07. Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization of the complex in dry ethanol, which contained less water molecules.

Crystal data for $\mathbf{1} \cdot (ClO_4)_6 \cdot 26H_2O$: $[Cu_6(Acntb)_6](ClO_4)_6 \cdot 26H_2O$, $M_r = 4233.39$, cubic, space group $Pa\bar{3}$ (no. 205), $a = 27.656(2)$ Å, $V = 21153(3)$ Å^3, $Z = 4$, crystal size $0.22 \times 0.16 \times 0.16$ mm^3, 61885 reflections measured, final $R1 = 0.0616$ and $wR2 = 0.1549$ for 2299 observed ($I > 2\sigma(I)$) reflections. The perchlorate anion is orientationally disordered with half-site occupancy. Anisotropic thermal factors were assigned to all the non-hydrogen atoms, while isotropic hydrogen atoms of Acntb$^-$ were included in structure factor calculation. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155221. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: January 9, 2001 [Z 16392]

  0044-8249/01/11309-1777 $ 17.50+.50/0

[1] a) M. J. Zaworotko, *Angew. Chem.* **2000**, *112*, 3180 – 3182; *Angew. Chem. Int. Ed.* **2000**, *39*, 3052 – 3054; b) D. M. L. Goodgame, D. A. Grachvogel, D. J. Williams, *Angew. Chem.* **1999**, *111*, 217 – 219; *Angew. Chem. Int. Ed.* **1999**, *38*, 153 – 156; c) I. M. Müller, T. Röttgers, W. S. Sheldrick, *Chem. Commun.* **1998**, 823 – 824.

[2] a) Y. Shin, J. Liu, L.-Q. Wang, Z. Nie, W. D. Samuels, G. E. Fryxell, G. J. Exarhos, *Angew. Chem.* **2000**, *112*, 2814 – 2819; *Angew. Chem. Int. Ed.* **2000**, *39*, 2702 – 2707; b) O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703 – 706; c) V. A. Russell, C. C. Evans, W. Li, M. D. Ward, *Science* **1997**, *276*, 575 – 579.

[3] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**, pp. 139 – 198; b) C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289 – 299; c) D. Phip, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242 – 1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154 – 1196.

[4] a) M. J. Zaworotko, *Angew. Chem.* **1998**, *110*, 1269 – 1271; *Angew. Chem. Int. Ed.* **1998**, *37*, 1211 – 1213; b) L. Carlucci, G. Giani, M. Moret, D. M. Proserpio, S. Rizzato, *Angew. Chem.* **2000**, *112*, 1566 – 1570; *Angew. Chem. Int. Ed.* **2000**, *39*, 1506 – 1510; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1588 – 1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1461 – 1494.

[5] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853 – 908, and references therein.

[6] a) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417 – 425; b) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794 – 796.

[7] a) B. F. Abrahams, S. J. Egan, R. Robson, *J. Am. Chem. Soc.* **1999**, *121*, 3535 – 3536; b) M. Scherer, D. L. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1690 – 1694; *Angew. Chem. Int. Ed*. **1999**, *38*, 1587 – 1592; c) R.-D. Schnebeck, E. Freisinger, B. Lippert, *Angew. Chem.* **1999**, *111*, 235 – 238; *Angew. Chem. Int. Ed*. **1999**, *38*, 168 – 170.

[8] S. B. Copp, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun*. **1993**, 1078 – 1079.

[9] H. Li, A. Laine, M. O'Keefe, O. M. Yaghi, *Science* **1999**, *283*, 1145 – 1147.

[10] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148 – 1150.

[11] a) C.-Y. Su, B.-S. Kang, Q.-G. Wang, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **2000**, 1831 – 1833; b) C.-Y. Su, B.-S. Kang, Q.-C. Yang, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **2000**, 1857 – 1862; c) C.-Y. Su, B.-S. Kang, H.-Q. Liu, Q.-G. Wang, T. C. W. Mak, *Chem. Commun*. **1998**, 1551 – 1552.

[12] "PLATON program:" A. L. Spek, *Acta Crystallogr. Sect.* A **1990**, *46*, 194 – 201.

[13] IR (KBr): $\tilde{\nu}$ = 3396, 3067, 1626, 1543, 1497, 1476, 1452, 1385, 1278, 1115, 1086, 747, 627 cm^{-1}; elemental analysis (%) found: C 42.37, H 5.11, N 13.12.

[14] IR (KBr): $\tilde{\nu}$ = 3432, 3067, 1697, 1626, 1543, 1498, 1476, 1452, 1386, 1278, 1114, 1088, 748, 628 cm^{-1}; elemental analysis (%) found: C 46.12, H 4.85, N 13.22, possibly corresponding to $[Cu_6(Acntb)_6](ClO_4)_6 \cdot 22H_2O \cdot 6(CH_3COCH_3)$, calcd: C 46.34, H 4.74, N 13.04.

[15] M. Moon, I. Kim, M. S. Lah, *Inorg. Chem.* **2000**, *39*, 2710 – 2711.

[16] K. D. Benkstei, J. T. Hupp, C. L. Stern, *Angew. Chem.* **2000**, *111*, 235 – 238; *Angew. Chem. Int. Ed*. **2000**, *39*, 2891 – 2893.

Toward Fully Synthetic Homogeneous Glycoproteins: A High Mannose Core Containing Glycopeptide Carrying Full H-Type 2 Human Blood Group Specificity**

Zhi-Guang Wang, Xufang Zhang, Michael Visser, David Live, Andrzej Zatorski, Ulrich Iserloh, Kenneth O. Lloyd, and Samuel J. Danishefsky*

Carbohydrate domains in the context of glycolipids and glycoproteins carry significant messages. The definition of the full scope and impact of oligosaccharide-based bioinformatics, falls within the scope of the rapidly growing field of glycobiology.[1] The sorting out of the diverse effects of glycosylation on phenomena ranging from protein folding[2] to cascades with a bearing on fertilization,[3] inflammation,[4] and metastasis,[5] constitutes a major challenge to glycobiology.[6] Other phenomena that are communicated in the "grammar" of carbohydrate structure include aberrant glycosylation patterns, associated with tumorigenesis, and blood typing.[7] The most widely known of the carbohydrate-centered serology systems, the ABO classification, is based on structural patterns of cell-surface glycoproteins on erythrocytes.[8]

From the perspective of chemistry, one of the issues complicating molecular level understanding of the consequences of glycoarchitecture is the phenomenon of heterogeneity. While the various carbohydrate domains present on a glycoprotein may be isolated and purified, this tends to be feasible only after detachment of the oligosaccharide ensemble from its macromolecular setting. One method for dealing with the issue of the inhomogeneity of glycoproteins is through synthesis—either chemical, enzymatic, or a combination of both.[9]

A long-term goal of our laboratory has been the development of methodology and strategies which would enable the synthesis of complex oligosaccharides bearing the inherent information in a context that simulates the natural glycoprotein setting. As will be shown below, advances in the field are

[*] Prof. S. J. Danishefsky,[+] Dr. Z.-G. Wang, X. Zhang, Dr. M. Visser, Dr. A. Zatorski, Dr. U. Iserloh
The Laboratory for Bioorganic Chemistry
Sloan – Kettering Institute for Cancer Research
1275 York Avenue, Box 106, New York, NY 10021 (USA)
Fax: (+1) 212-772-8691

Dr. D. Live
The Department of Biochemistry, Molecular Biology, and Biophysics
University of Minnesota, Minneapolis, MN 55455 (USA)

Dr. K. O. Lloyd
The Laboratory for Tumor Antigen Immunochemistry
Sloan – Kettering Institute for Cancer Research
1275 York Avenue, New York, NY 10021 (USA)

[+] The Department of Chemistry
Columbia University, Havemeyer Hall, New York, NY 10027 (USA)

[**] This work was supported by the National Institutes of Health (Grant nos.: HL-25848 and CA-28824 (to S.J.D.), and CA-710506 (to K.O.L.)). Postdoctoral fellowship support is gratefully acknowledged by Z.-G.W. (US Army breast cancer grant no.: DAMD17-97-1-7119) and M.V. (NIH grant no.: CA-62948-04). We gratefully acknowledge Dr. George Sukenick of the Sloan – Kettering Institute's NMR core facility for mass spectral and NMR spectroscopic analyses (SKI core grant no.: CA-08748).

  0044-8249/01/11309-1778 $ 17.50+.50/0