Self-Assembly of Pyrazolyl Based Ligands and Silver Cation into Metallamacrocycles and Tubular Coordination Networks

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The 2,6-bis(pyrazolyl)pyrazine ligand **1** forms a 2,2-metallamacrocycle **3**, composed of two ligands and two cations, in the presence of the Ag^+ cation. In the crystalline phase, the 1,3,5-tris(pyrazolyl)benzene ligand **2** leads to an infinite metallatubular network in the presence of the Ag^+ cation, composed of the 2,2-metallamacrocycle **4**, which is formed from two molecules of **2** and two cations. This infinite network is formed by double interconnection of consecutive metallamacrocycles through binding of Ag^+ centers by the free pyrazolyl moieties.

For the last decade, much attention has been focused on the formation of metallamacrocycles,[1] and many bis-monodentate ligands such as 4,4′-bipyridine, pyrimidine, bipyrazine, 4,7-phenanthroline or bis-pyridines interconnected by rigid or flexible spacers have been shown to form a variety of metallamacrocycles.[2] Recently, we have reported the formation of silver and palladium 2,2-metallamacrocycles using ligands based on two *p*-dialkylaminopyridine units connected by aliphatic chains of variable length.[3]

A further development in this area could be the formation, using self-assembly processes, of coordination molecular networks based on the interconnection of metallamacrocycles by coordination bonds. As schematically represented in Figure 1, one can design tridentate ligands in which two coordination sites are positioned in such a manner that, in the presence of divalent metal cations, they form 2,2-metallacycles composed of two metals and two ligands; the remaining coordination site would then serve as a connecting center allowing binding to another divalent metal cation and the formation of infinite 1-D networks. This strategy has been demonstrated by using terpyridine ligands bearing a thioether group.[4]

In order to investigate this possibility, ligand **1** was designed, synthesized and structurally characterized in the crystalline phase by X-ray diffraction on a single crystal. Indeed, ligand **1**, based on a pyrazine moiety bearing two pyrazolyl groups at the 2 and 6 positions, may fulfil the above criteria if the two pyrazolyl units and the N4 nitrogen atom of the pyrazine unit participate in the binding of linearly coordinated metal centers. However, **1** can also act either as a tridentate chelating ligand if the N1 nitrogen atom of the pyrazine ring was acting as coordination site in conjunction with the two pyrazolyl groups, or as a tetradentate ligand if, in addition to the two pyrazolyl moieties, both nitrogen atoms of the pyrazine ring were participating in the bonding of metal centers.

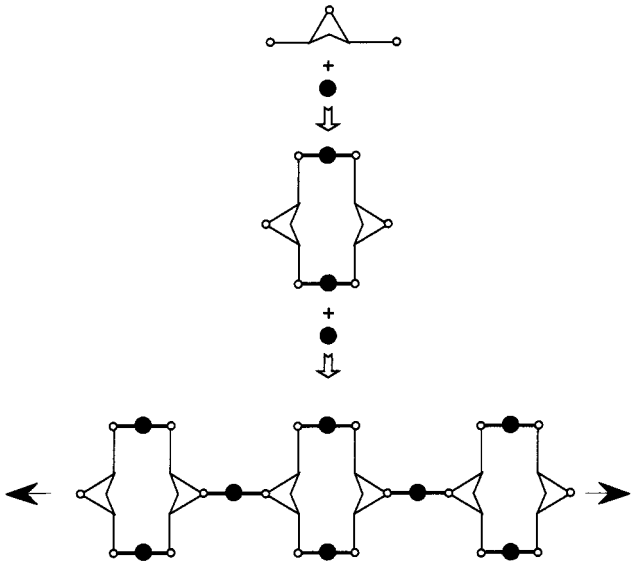

Figure 1. Schematic representation of an infinite coordination network based on interconnection of 2,2-metallamacrocycles by bridging metal centers

Ligand **1** was prepared in 77% yield upon coupling the sodium salt of pyrazole with 2,6-dichloropyrazine in DMF. The pyridine analogue of **1** and its Ru(II)[5] and Cu(II)[6] complexes have previously been reported. The solid state structure of **1** (Figure 2) was determined by an X-ray diffraction study which revealed the following features. In the solid state, the free ligand **1** possesses a plane of symmetry and adopts an almost planar conformation with an N1−N2−C5−N3 dihedral angle of 171.6°. Both the N1 and N1′ atoms are in a trans configuration with respect to N3. Whereas the C5−N2 bond length is 1.4000 Å, the C5−N3 bond is much shorter (1.324 Å), as expected; the N1−N2 bond length is 1.362 Å.

In an attempt to form infinite 1-D networks based on the interconnection of metallamacrocycles, the binding of the

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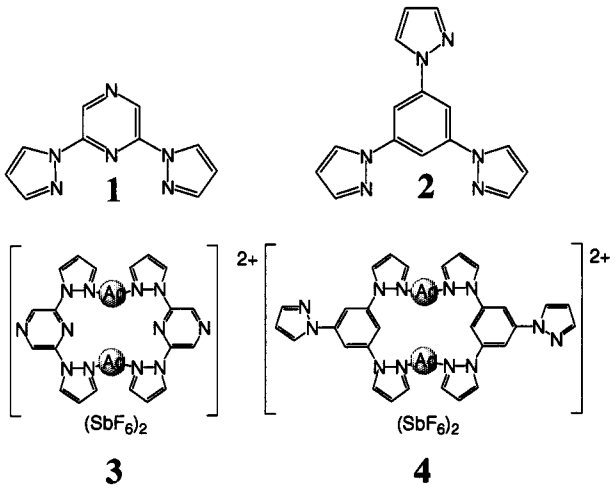

Scheme 1

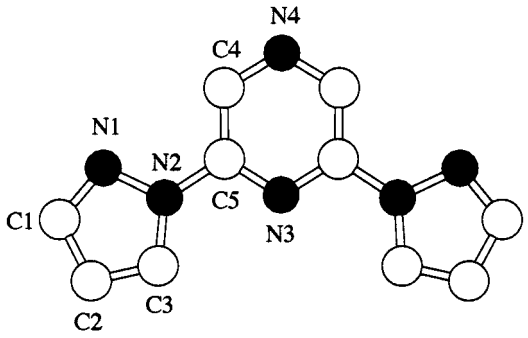

Figure 2. X-ray structure of the free ligand **1** (Table 1); hydrogen atoms omitted for clarity; for bond lengths and angles see text

Ag^+ cation by the ligand **1** was investigated. The Ag^+ cation was selected because, firstly, it forms kinetically labile complexes with nitrogen-containing ligands and, secondly, it may adopt a linear coordination geometry. Indeed, we have previously obtained a silver 2,2-metallamacrocycle in which the Ag^+ cation is linearly coordinated to two nitrogen atoms.[3] However, other types of coordination geometry, in particular trigonal or tetrahedral, are commonly observed. In this case, infinite 1-D linear[7] or helical[8] silver coordination networks in which the cation acts as a tetrahedrally connecting center, were obtained.

Upon reacting equimolar amounts of ligand **1** and $AgSbF_6$in $CHCl_3$/EtOH (1:3) at room temperature, the binuclear silver metallamacrocycle **3** was obtained in 70% yield (Scheme 1). The structure of **3** was investigated by an X-ray diffraction study (Table 1) on a single crystal (see Figure 3). The crystal is exclusively composed of discrete 2,2-metallamacrocycles **3** and SbF_6^- anions; the cationic part is a binuclear silver complex composed of two ligands and two Ag^+ cations forming a 2,2-metallamacrocycle. The latter is formed by the bridging of two pyrazolyl moieties of the ligand by two silver atoms, implying that **1** behaves as a bidentate unit. For ligand **1**, the pyrazolyl and the pyrazine units are tilted by −21.6°. The two ligands are not coplanar but twisted, thus leading to a rather short Ag−Ag distance of 2.911 Å. Both silver cations are almost linearly coordinated (N−Ag−N angle of 178.2°) to two pyrazolyl nitrogen atoms with a N−Ag distance of 2.160 Å. The SbF_6^- anions are neither disordered nor in specific interactions with the cationic units. The formation of such a metallamacrocycle is not unprecedented, analogous structures were obtained from Cu^I and benzimidazole-based ligands,[9] and bis-pyridine and Ag^I.[10] Attempts to generate the desired infinite coordination network by increasing the Ag^+/**1** stoichiometry and by varying the crystallization conditions have so far been unsuccessful.

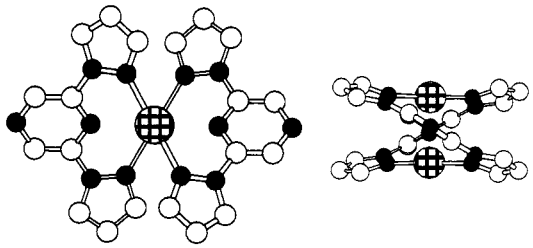

Figure 3. X-ray structure of the metallamacrocycle **3** {projection along the Ag-Ag axis (left) and lateral view (right)} obtained under self-assembly conditions between **1** and the Ag^+ cation (Table 1); hydrogen atoms and anions omitted for clarity; for bond lengths and angles see text

Tubular structures are interesting architectures, in particular with respect to their ability to transport ions or molecules. In principle, such structures may be obtained either from nonreversible covalent bonds, or other types of reversible interactions such as H-bonding or stacking processes. It has been shown that tubular systems may be formed by 1-D chains adopting a helical structure, as observed for polypeptides in natural systems,[11][12] or for helical coordination polymers;[8][13] by interconnection of ring modules as, for example, for cyclic peptides;[11][12] by stacks of cyclic units in the liquid crystalline phase;[14] by poly-[15] or oligomeric[16] structures bearing ring systems; or by rolling up 2-D sheets such as graphite leading to carbon nanotubes.[17] Following the above strategy for the formation of 1-D coordination networks based on the interconnection of metallamacrocyclic units, we reasoned that, by an appropriate choice of ligands, it should be possible to generate tubular coordination networks using the self-assembly strategy based on the formation of reversible coordination bonds. Indeed, the appropriate interconnection of metallamacrocycles may lead to a variety of tubular systems. An example of such an architecture, based on the mutual interconnection of metallamacrocycles, is schematically represented in Figure 4. The formation of such a structure requires a ligand and metal-cation pair allowing the reversible formation of metallamacrocycles and their mutual interconnection (Figure 4). This strategy was demonstrated using terpyridine ligands bearing a thioether group.[9]

We believed that the tridentate ligand **2** composed of three pyrazolyl moieties located in the 1, 3 and 5 positions of a benzene ring might be an interesting unit for the formation of a metallatubular 1-D coordination network. Compound **2**[18] and its 1,3,5-triazine[19] and 1,3,5-(pyrazolyl-1-methyl)[20] analogues have previously been reported. With

Table 1. Single crystal X-ray data for ligand **1** and the silver complexes **2** and **3**[a]

	1	**3**	**4**
Formula	$C_{10}H_8N_6$	$C_{10}H_8AgN_6{\cdot}SbF_6$	$C_{15}H_{12}AgN_6{\cdot}SbF_6$
Molecular weight	212.22	555.83	619.91
Crystal system	Monoclinic	Orthorhombic	monoclinic
Space group	*P*nma	*C*cca	*C*12/*c*1
a(Å)	11.8450(4)	10.3373(2)	22.873(1)
b(Å)	21.3300(9)	14.0278(3)	12.8220(5)
c(Å)	3.8290(4)	21.6100(4)	16.867(1)
β(deg)	89.972(2)	3133.7(2)	128.256(1)
V(Å^3)	967.4(2)		3884.4(6)
Z	4	8	8
Color	colorless	colorless	colorless
Crystal dim. (mm)	0.17 × 0.13 × 0.10	0.20 × 0.15 × 0.08	0.20 × 0.20 × 0.10
D(calc) (g cm^{-3})	1.46	2.36	2.12
F(000)	440	2096	2368
μ(mm^{-1})	0.098	3.045	2.469
Temperature (K)	173	294	294
h/*k*/*l* limits	0,4/−16,16/−30,30	0,14/0,19/0,29	0,35/0,15/−25,20
Theta limits(deg)	2.5/30.55	2.5/29.56	2.5/34.35
Number of data measured	6478	13952	14796
Number of data with $I > 3\ \sigma(I)$	1285	1604	3569
R	0.041	0.050	0.046
R_w	0.053	0.064	0.071
GOF	1.042	1.008	1.355

[a] Radiation: Mo-K_α graphite monochromated; wavelength (Å): 0.71073; diffractometer: KappaCCD; scan mode: phi scans

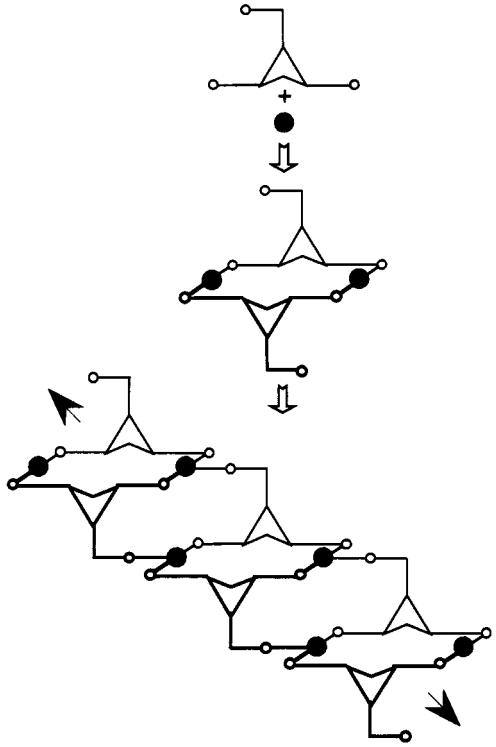

Figure 4. Schematic representation of an infinite coordination tubular network based on mutual interconnection through coordination bonds of consecutive 2,2-metallamacrocycles

respect to the bridging metallic center, the above mentioned strategy requires a tricoordinated metal adopting a T-type coordination geometry. Again, we believed that the Ag^+ cation was the best candidate.

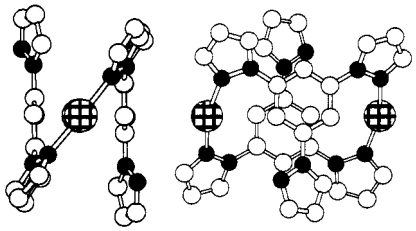

Figure 5. The X-ray structure of the metallamacrocycle **4** composed of **2** and the Ag^+ cation (Table 1). Projection along the Ag-Ag axis (left) and lateral view (right). H atoms and anions are not presented for clarity. For bond lengths and angles see text

Upon slow diffusion in the dark and at room temp. of a solution of **2** in $CHCl_3$ into an EtOH solution of $AgSbF_6$, colorless crystals were obtained after three days which were studied by X-ray diffraction (Table 1). The crystal (Figures 5 and 6), consisting exclusively of ligand **2**, Ag^+ cations and SbF_6^- anions, is composed of parallel cationic metallatubular coordination networks and the SbF_6^- anion. The formation of the tubular structure results from the mutual bridging of the binuclear silver 2,2-metallamacrocycles **4**, (Scheme 1), composed of two Ag^+ cations and two ligands **2** and analogous to the metallamacrocycle **3** obtained with ligand **1**. For the formation of the metallamacrocyclic unit **4** (Figure 5) within each of the two tridentate ligands **2**, two out of three pyrazolyl units are bridged by two Ag^+ cations, the remaining two pyrazolyl units, located at each end of the cyclic structure and pointing in opposite directions with respect to the plane defined by the metallamacrocycle, serve to interconnect consecutive cyclic units (Figure 6). Dealing

with the ligand **2**, the three pyrazolyl moieties are tilted by −41.2°, 32.4° and 23.0° with respect to the phenyl ring, respectively. For the metallamacrocycle **4**, the N−Ag and Ag−Ag distances are 2.150 Å, 2.154 Å and 7.785 Å, respectively. As stated above, the metallamacrocycles are mutually and doubly interconnected (Figure 6) by the third pyrazolyl on each ligand **2** with a rather long N−Ag distance of 2.620 Å; thus the overall coordination geometry around the Ag^+ cation may be described as severely distorted trigonal (T-type) with N−Ag−N angles of 162.4°, 99.0° and 98.6°. As in the case of **3** mentioned above, the SbF_6^- anions were neither disordered nor in specific interactions with the cationic units. Although in terms of topology the network formed may be described as tubular, due to the size of the metallamacrocyclic unit, the internal space within each tubular network is exceedingly small.

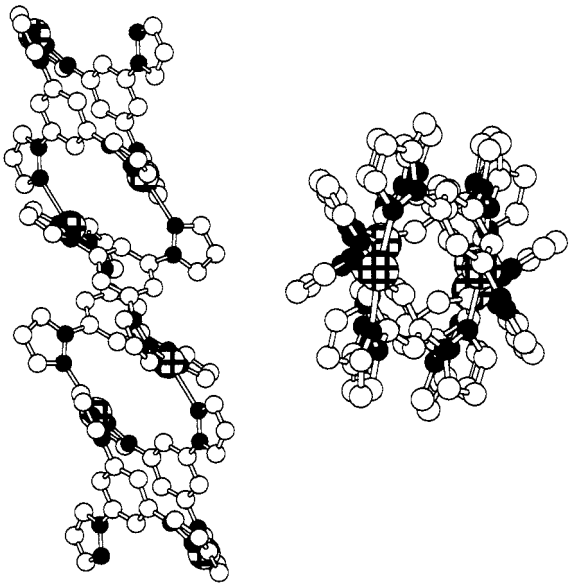

Figure 6. A portion of the X-ray structure showing the formation of the metallatube {parallel (left) and perpendicular (right) views} between the tridentate ligand **2** and Ag^+ cations; hydrogen atoms and anions omitted for clarity

In conclusion, from ligand **1**, bearing two pyrazolyl units, and the Ag^+ cation, both in solution and in the solid state, the formation of a binuclear silver 2,2-metallamacrocycle was achieved and its solid structure was elucidated by X-ray diffraction on a single crystal. With the Ag^+ cation and ligand **2** containing three pyrazolyl, units, the formation of a 1-D tubular coordination network was observed in the solid state by X-ray diffraction on a single crystal. The tubular coordination network results from the mutual interconnection of metallamacrocycles through N−Ag coordination bonds. Due to the size of the metallamacrocyclic unit, the internal size of the tubular architecture obtained was exceedingly small, thus precluding any possible application in terms of its use as a channel. However, increasing the size of the metallamacrocycle by using larger ligands such as 1,3,5-tris(phenylpyrazol)ylbenzene, one might be able to generate tubular networks with sufficient internal space. This type of architecture, due to its cationic nature, may be of interest for the transport of anions, which remains a challenge. Work along these lines is currently in progress

Experimental Section

Synthesis of Ligand 1: To a suspension of pyrazole (274 mg, 4 mmol) in DMF (35 mL) was added NaH (168 mg, 4.22 mmol) and the mixture stirred under argon at 50°C for 20 minutes. To this suspension was added 2,6-dichloropyrazine (300 mg, 2 mmol) and the resulting yellow mixture was heated to 90°C under argon and stirred for a further 12 hours before it was allowed to cool to room temperature. Upon pouring the suspension into cold water, the desired compound **1** was obtained in 77% yield (330 mg) as a white solid which was filtered and further washed with water. m.p. 180−181°C. − ^{1}H NMR (300 MHz, 25°C, [D$_6$]acetone): δ = 6.66 (dd, *J* = 1.3, 2.7 Hz, 2 H, pyrazole), 7.89 (d, *J* = 1.5 Hz, 2 H, pyrazol), 8.84 (d, *J* = 1.5 Hz, 2 H, pyrazole), 9.14 (s, 2 H, pyrazine). − ^{13}C NMR (75.46 MHz, 25°C, $CDCl_3$): δ = 108.8, 127.3, 131.5, 143.3, 144.8. − UV (25°C, $CHCl_3$) λ_{max} (ε mol^{-1}lcm^{-1}): 270 (18400), 327 (29200) nm. − FAB$^{+\ m/z}$ (%) = 212.1 (100%).

Synthesis of the Binuclear Silver Complex 3: Stirring an equimolar mixture of **1** and $AgSbF_6$ (0.23 mmol) in $CHCl_3$/EtOH (1:3) for 5 hours at room temperature in the dark under argon, gave the binuclear silver complex **3** in 80% yield as a white powder which was filtered, washed with CH_2Cl_2 and EtOH and dried. m.p. 240°C (decomposition). − ^{1}H NMR (300 MHz, 25°C, [D$_6$]acetone): δ = 6.83 (dd, *J* = 2.0, 2.7 Hz, 2 H, pyrazole), 7.87 (d, *J* = 1.9 Hz, 2 H, pyrazole), 8.96 (d, *J* = 3.0 Hz, 2 H, pyrazole), 9.40 (s, 2 H, pyrazine). − ^{13}C NMR (75.46 MHz, 25°C, $CDCl_3$): δ = 111.1, 131.2, 134.1, 143.8, 145.2. − FAB$^{+\ m/z}$ (%) = 874.9 (100%, **3**-SbF_6).

Acknowledgments

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[1] M. Fujita in *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, **1996**, *Vol. 9* (Eds. J. P. Sauvage, M. W. Hosseini), p. 253; J. K. M. Sanders, in *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, Pergamon, **1996**, *Vol. 9* (Eds. J. P. Sauvage, M. W. Hosseini), p. 131; R. W. Saalfrank, A. Stark, K. Peters, H.-G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851; P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; C. M. Drain, J.-M. Lehn, *J. Chem. Soc., Chem. Commun*. **1994**, 2313; T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084.

[2] C. V. Krishnamohan Sarma, S. T. Griffin, R. D. Rogers, *Chem. Commun*. **1998**, 215; R.-D. Schnebeck, L. Randaccio, E. Zangrando, B. Lippert, *Angew. Chem. Int. Ed.* **1998**, *37* 119; J. R. Hall, S. J. Loeb, G. K. H. Shimizu, G. P. A. Yap, *Angew. Chem. Int. Ed.* **1998**, *37*, 121.

[3] R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian, J. Fischer, *Chem. Commun*. **1998**,1625.

[4] M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun*. **1997**, 307; M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun*. **1997**, 1805.

[5] D. J. Jameson, J. K. Blaho, K. T. Kruger, K. A. Goldsby, *Inorg. Chem*., **1989**, *28*, 4314.

[6] N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies, M. A. Halcrow, *Angew. Chem. Int. Ed*. **1998**, *37*, 2221.

[7] G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas, J. Fischer, *Chem. Commun*. **1998**, 2545.

[8] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. White, *Angew. Chem. Int. Ed.* **1998**, *37*, 920.

[9] C. Piguet, G. Bernadinelli, A. F. Williams, *Inorg. Chem*. **1989**, *28*, 2920, S. Rüttimann, C. Piguet, G. Bernardinelli, B. Bocquet, A. F. Williams, *J. Am. Chem. Soc*. **1992**, *114*, 4230.
[10] C. M. Hartshorn, P. J. Steel, *Inorg. Chem*. **1996**, *35*, 6902.
[11] D. H. Lee, M. R. Ghadiri in *Comprehensive Supramolecular Chemistry* (Eds: J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vögtle), Pergamon, **1996**, *Vol. 9* (Eds. J.-P. Sauvage, M. W. Hosseini), p. 451; J. D. Lear, Z. R. Wasserman, W. F. DeGrado, *Science* **1988**, *240*, 1177.
[12] P. De Santis, S. Morosetti, R. Rizzo, *Macromolecules* **1974**, *7*, 52; M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. McRee, N. Khazanovich, *Nature* **1993**, *366*, 324.
[13] O. J. Gelling, F. van Bolhuis, B. L. Feringa, *J. Chem. Soc., Chem. Commun*. **1991**, 917, Y. Dai, T. J. Katz, D. A. Nichols, *Angew. Chem. Int. Ed. Engl*., **1996**, *35*, 2109; B. Wu, W.-J. Zhang, S.-Y. Yu, X.-T. Wu, *Chem. Commun*. **1997**, 1795.
[14] J.-M. Lehn, J. Malthête, A.-M. Levelut, *J. Chem. Soc., Chem. Commun*. **1985**, 1794; V. Percec, G. Johansson, J. A. Heck, G. Ungar, S. V. Betty, *J. Chem. Soc., Perkin Trans 1* **1993**, 1411, T. Komori, S. Shinkai, *Chem. Lett*. **1993**, 1455.
[15] U. F. Kragten, M. F. M. Roks, R. J. M. Nolte, *J. Chem. Soc., Chem. Commun*. **1985**, 1275; C. Mertesdorf, H. Ringsdorf, *Mol. Cryst. Liq. Cryst*. **1989**, *5*, 1757.
[16] J.-P. Behr, C. J. Burrows, R. J. Heng, J.-M. Lehn, *Tetrahedron Lett*. **1985**, *26*, 215; A. Nakano, Q. Xie, J. V. Mallen, L. Echegoyen, G. W. Gokel, *J. Am. Chem. Soc*. **1990**, *112*, 1287.
[17] S. Iijima, *Nature* **1991**, *354*, 56.
[18] H. Lexy, T. Kauffmann, *Chem. Ber*. **1980**, *113*, 2755.
[19] H. Reimlinger, A. Noels, J. Jadot, A. Van Overstraeten, *Chem. Ber*. **1970**, *103*, 1954.
[20] C. M. Hartshorn, P. J. Steel, *Chem. Commun*. **1997**, 541.

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