Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Solid State Calix[4]arene Tubular Assemblies Based on Cation-π Interactions

Jan Budka[a]; Pavel Lhoták[a]; Ivan Stibor[a]; Jan Sýkora[b]; Ivana Císařová[c]
[a] Department of Organic Chemistry, Institute of Chemical Technology, Prague, Czech Republic [b] Institute of Chemical Process Fundamentals, Prague, Czech Republic [c] Department of Inorganic Chemistry, Charles University, Prague, Czech Republic

To cite this Article Budka, Jan , Lhoták, Pavel , Stibor, Ivan , Sýkora, Jan and Císařová, Ivana(2003) 'Solid State Calix[4]arene Tubular Assemblies Based on Cation-π Interactions', Supramolecular Chemistry, 15: 5, 353 — 357

To link to this Article: DOI: 10.1080/1061027031000090055

URL: http://dx.doi.org/10.1080/1061027031000090055

Supramolecular Chemistry, 2003 Vol. 15 (5), pp. 353–357

Taylor & Francis
Taylor & Francis Group

Solid State Calix[4]arene Tubular Assemblies Based on Cation–π Interactions

JAN BUDKA[a], PAVEL LHOTÁK[a,*], IVAN STIBOR[a], JAN SÝKORA[b] and IVANA CÍSAŘOVÁ[c]

[a]*Department of Organic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic;* [b]*Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojová 135, 165 02 Prague 6, Czech Republic;* [c]*Department of Inorganic Chemistry, Charles University, Hlavova 8, 128 43, Prague 2, Czech Republic*

Received (in Southampton, UK) 9 December 2002; Accepted 16 January 2003

Infinite tubular assemblies based on calix[4]arenes can be easily constructed using cation–π interactions of silver triflate with preorganised aromatic subunits (*1,3-alternate* or *pinched cone* conformations). X-ray crystallographic analysis shows that the overall self-assembly is held together by triflate anions playing the role of the bridges between the individual complexes.

Keywords: Self-assembly; Calixarenes; Cation–π interactions; Crystallographic analysis

INTRODUCTION

Calix[4]arenes, the well-known family of macrocyclic compounds [1–4], play an important role as the building blocks or molecular scaffolds in the construction of more elaborate systems. The combination of their unique concave molecular architecture with a tuneable cavity shape makes calix[4]arenes ideal candidates for supramolecular chemistry, where the combination of the defined conformation, preorganisation of molecular shape, rigidity and suitable noncovalent interactions can lead to the design of very interesting assemblies.

Here we report the formation and characterization of the supramolecular self-assembly systems where calix[4]arenes, possessing cationnd–π interactions [5–7] with the silver cations, form infinite tubular [8–13] self-assemblies in the solid state.

The design of tubes is based on our previous finding [14], that biscalixarene **1** is able to complex the silver cation in the de-*tert*-butylated part of the molecule, which adopts C_{2v} symmetry (*pinched cone* conformation) suitable for the Ag^+ complexation. As shown by X-ray analysis, the Ag^+ is sandwiched by two coplanar aromatic units (double η^1 mode with strong cation–π interactions) while the remaining two coordination sites are occupied by the triflate oxygens. At the same time the triflates serve as the bridges [15–21], connecting the two individual complexes to the dimeric structure as indicated in Fig. 1. Hence, the exploitation of the above-described structural motif using the biscalixarene structure **2** could lead to infinite structures in the solid state.

RESULTS AND DISCUSSION

The synthesis of **2** was accomplished using modification of the literature method [22]. The condensation of the corresponding calixarene–tetratosylate with calix[4]arene in the presence of K_2CO_3 gave the proposed product in 16% yield after preparative TLC separation.

The crystallization of **2** with 2.5 equivalents of AgTfl from a $CHCl_3$–ethyl acetate mixture gave crystals suitable for single crystal X-ray analysis. As shown in Fig. 2, biscalixarene **2** interacts with the Ag^+ cation on both sites of the molecule exhibiting again a double η^1 binding mode. The Ag^+ is situated almost symmetrically in the middle of the cavity ($C5{-}Ag = 2.45\,\text{Å}$, $C17{-}Ag = 2.42\,\text{Å}$, angle $C5{-}Ag{-}C17 = 168.35°$). To saturate the requirements of the Ag^+ coordination sphere (pseudo tetrahedral arrangement), the two remaining positions are occupied by the two triflate oxygens. The Ag–O distances ($Ag{-}O42 = 2.48\,\text{Å}$, $Ag{-}O43' = 2.52\,\text{Å}$) are longer than the corresponding C–Ag distances indicating

---

*Corresponding author. E-mail: lhotakp@vscht.cz. Fax: +420-2-2435 4288. Tel.: +420-2-2435 4280.

ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/1061027031000090055

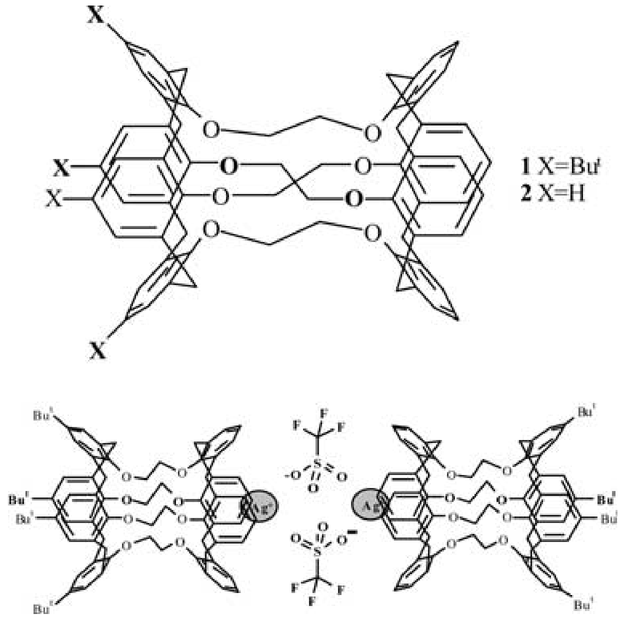

FIGURE 1 Structural formulae of compounds **1** and **3** with schematically depicted complex of **1** with silver triflate.

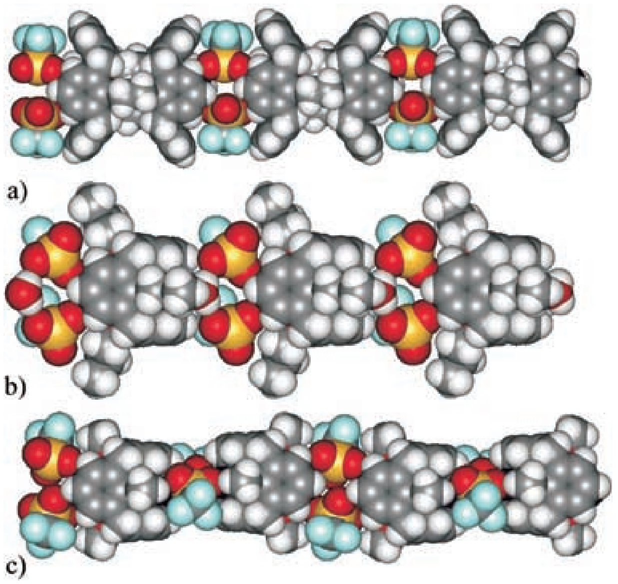

FIGURE 3 Infinite tubular self-assembly in (a) **2**·AgTfl complex; (b) **3**·AgTfl complex; (c) **4**·AgTfl complex, (space filling presentation of X-ray structures).

strong interactions with both aromatic systems (Fig. 2). The neighbouring calixarene–Ag$^+$ complexes are then tethered together by the triflate bridges creating finally the infinite tube-like structures in the crystal lattice (Fig. 3a).

The success with the biscalix[4]arene structure led us to the idea of using a less complicated system for the design of the infinite tubes. Such a molecule should be ditopic (double Ag$^+$ complexation), linear and rigid to ensure suitable mutual positions in the overall self-assembly. 1,3-*alternate* Calixarenes seemed to be suitable candidates for this role. Unfortunately, to the best of our knowledge, there is no precedent in the literature dealing with the crystal structure of a 1,3-*alternate* calixarene–Ag$^+$ complex. Shinkai *et al.* [23] published an X-ray structure of a *partial cone*–Ag$^+$ system, where the silver cation is trapped by two opposite aromatic rings with the contribution of the phenolic oxygen from the inverted aromatic unit (Fig. 4a). Based on this finding, the authors proposed a similar binding mode for a 1,3-*alternate* [24,25], using two aromatic rings and two phenolic oxygens (Fig. 4b).

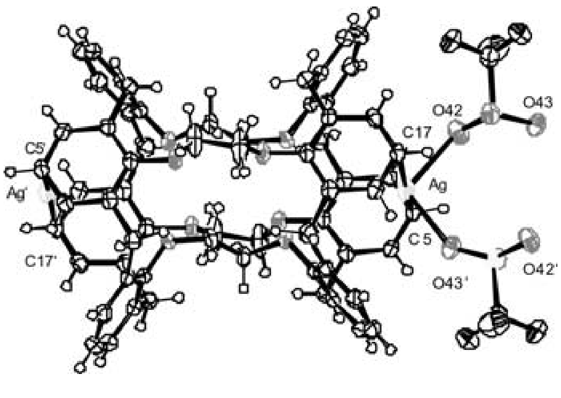

FIGURE 2 ORTEP drawing of **2**·AgTfl complex. Thermal ellipsoids are scaled at 50% probability level.

It is known [24–26] that 25,26,27,28-tetrapropoxycalix[4]arene 1,3-*alternate* **3** exhibits high ionophoricity with π-donor participation in the cation binding. It was believed [23–26] that calixarene **3** solely formed the 1:1 complex with the silver cation which would exclude the use of this conformer for the infinite channel design. Fortunately, during our reinvestigation of similar systems we found that compound **3** interacts with AgTfl in a 1:2 ratio in the solid state. The final evidence for 1:2 binding was obtained by X-ray crystallography which showed that spontaneously formed infinite channels based on the Ag$^+$–π interactions can be found.

As shown in Fig. 5a, one half of the self-assembled structure resembles the situation with **2** (η^1 binding mode with one Ag$^+$ cation being situated almost symmetrically between two *para* positions of calixarene (C23–Ag2 = 2.44 Å, C11–Ag2 = 2.43 Å, angle C23–Ag2–C11 = 166.06°) and exhibiting two interactions with triflate oxygens (2.46 and 2.54 Å)). Interestingly, the second silver cation adopts a different binding mode. The Ag$^+$ is again sandwiched by two coplanar aromatic units, but this time is sitting approximately between the centres of the two opposite aromatic bonds which are 4.88 Å apart (i.e. double η^2 binding mode). Tetrahedral arrangement of the Ag$^+$ coordination sphere is completed by the interaction with oxygen atom from propoxy

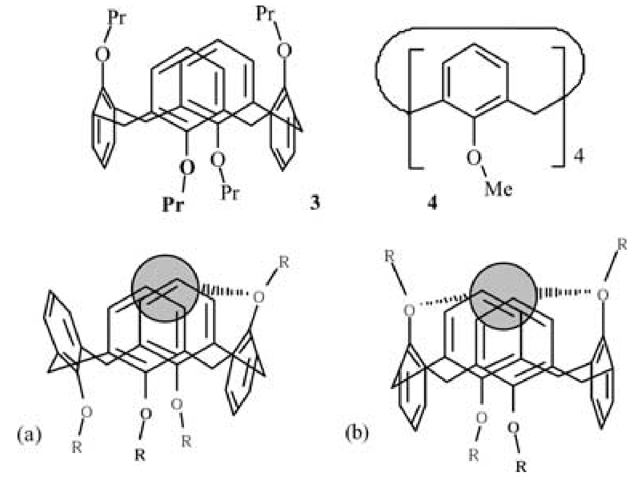

FIGURE 4 Structural formula of compounds **3** and **4**. Schematically depicted; (a) binding mode observed [23] in *partial cone* conformer; (b) binding mode proposed [24,25] for 1,3-*alternate*.

group (O29–Ag1 = 2.61 Å) and with one molecule of water (Ag1–O50 = 2.35 Å). This water molecule, presumably originated from the ethyl acetate used for the crystallisation, plays a key role in the self-assembly arrangement. It enables two triflate units to be held by hydrogen bonds (H501–O52 = 1.90 Å, H502–O62 = 1.92 Å) in the correct position for the formation of bridges with the silver cation from the neighbour molecule (Fig. 5b). Thus, the whole structure of the infinite channel is held by an array of cation–π interactions, hydrogen bonds and triflate bridges (Fig. 3b).

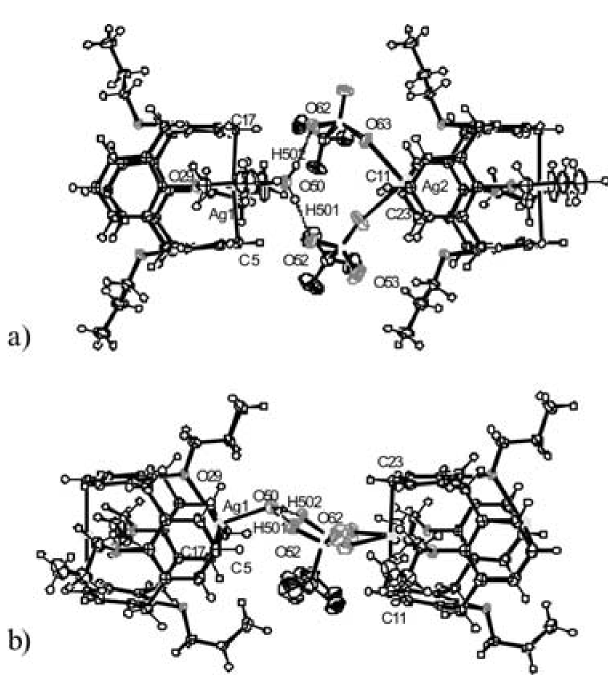

FIGURE 5 ORTEP drawing of **3**·AgTfl complex showing the binding mode via water molecule (O50). Thermal ellipsoids are scaled at 50% probability level.

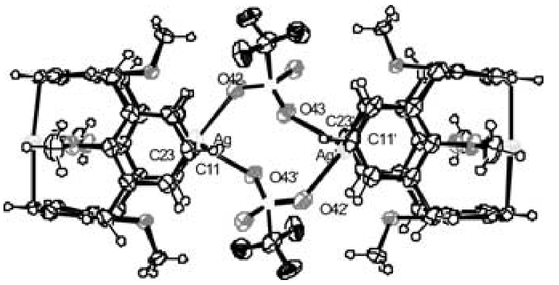

FIGURE 6 ORTEP drawing of **4**·AgTfl complex. Thermal ellipsoids are scaled at 50% probability level.

To test the general applicability of the above-mentioned design with conformationally mobile derivatives we have used the 25,26,27,28-tetramethoxycalix[4]arene **4**. This compound has already been reported in the literature [27] to create a discrete 1:1 complex with $AgNO_3$ in the solid state where the molecule adopts a *partial cone* conformation (Fig. 4a). On the other hand, it is well documented that the triflate anion is a much stronger bridging unit than NO_3^- in the case of Ag^+ complexes [15–21]. Consequently, the slow evaporation of an ethyl acetate solution of **4**–AgTfl 1:2.5 (molar ratio) mixture gave monocrystals of infinite channels based on a double η^1 binding mode. Two Ag^+ cations are again held at both sites of a 1,3-*alternate* by the interactions with opposite aromatic units (C23–Ag = 2.47 Å, C11–Ag = 2.47 Å, C23–Ag–C11 = 166.41°). The individual calixarene molecules are then interconnected via two triflate bridges (O–Ag = 2.46 and 2.86 Å) resembling the situation in biscalixarene **2** (Fig. 6). Interestingly, in the case of tetramethoxycalix[4]arene **4** no water molecule (as found in the propoxy derivative **3**) is required to keep the connection. Obviously, the sterical requirements of methoxy substituents are much lower than those of the corresponding propoxy groups, thus enabling direct bridging via triflate anions.

It is noteworthy that the binding modes observed in the crystallographic structures of the complexes do not correspond to those proposed in the literature (Fig. 4b). Fig. 7 summarises the situation for compounds **2**, **3** and **4**. It is evident that the silver cation is much more strongly held by the oxygen atoms of the triflate anion (7b, 7c) than by the oxygen atoms of the inverted alkoxy groups. Thus, one of the binding modes for 1,3-*alternate* **3** almost completely resembles that of the *cone* derivative **2** (compare Figs. 7c and 7a) where stabilisation from the alkoxy groups is impossible. The proposed complexation via interactions with both alkoxy groups has not been found.

In summary, we have demonstrated the role of the cation–π interactions in the rational design of supramolecular self-assembled systems.

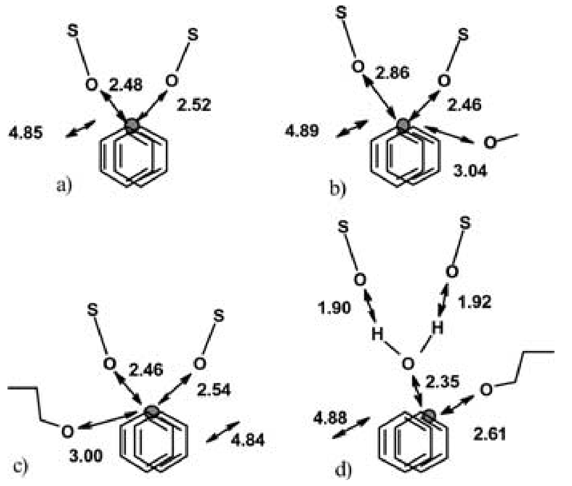

FIGURE 7 The binding modes found for: (a) compound **2**; (b) compound **4**; (c) compound **3** (first binding mode); (d) compound **3** (second binding mode). Silver atoms are shaded. All distances are in Å.

The combination of suitably preorganised π-electron-rich calix[4]arene cavities and the silver cation–π interactions offers many possibilities for the simple construction of infinite tubes in the solid state. Further research on Ag^+–π interactions is currently underway in our laboratory.

EXPERIMENTAL

Suitable monocrystals of derivatives **2**, **3** and **4** were grown by slow evaporation of ethyl acetate–dichloromethane solutions with 3 equivalents of silver triflate added. Data were measured at 150(2) K on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation [28]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-178421, CCDC-178418 and CCDC-186670. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk].

X-ray data for **2**: $2AgCF_3SO_3 \cdot C_{64}H_{56}O_8 \cdot 2CHCl_3$, $M = 1705.75\,\mathrm{g\,mol^{-1}}$, triclinic system, space group $P\bar{1}$, $a = 12.144(1)$, $b = 12.536(1)$, $c = 12.885(1)$ Å, $\alpha = 70.993(1)$, $\beta = 62.624(1)$, $\gamma = 84.040(1)$, $Z = 1$, $V = 1644.5(1)\,\text{Å}^3$, $D_c = 1.72\,\mathrm{g\,cm^{-3}}$, μ(Mo–Kα) $= 9.87\,\mathrm{mm^{-1}}$, crystal dimensions of 0.2 × 0.3 × 0.4 mm. 32258 reflections were integrated ($\theta_{max} = 27.48°$). The structure was solved by direct methods [29]. The whole structure was refined anisotropically by full matrix least-squares on F values [30] to final $R = 0.040$ and $Rw = 0.041$ ($\Delta\rho_{max} = 0.85$ and $\Delta\rho_{min} = -0.71\,\mathrm{e}\,\text{Å}^{-3}$) using 557 parameters for 6211 independent reflections with $I > 1.96\sigma(I)$. It was inevitable to model disorder of ethoxy-bridges. Hydrogen atoms of these bridges were located from the expected geometry and were placed only to carbon atoms with an occupancy higher than 0.1. They were not refined. The remaining hydrogen atoms were found from a Fourier map and expected geometry and their positions and isotropical temperature factors were refined.

X-ray data for **3**: $2AgCF_3SO_3 \cdot C_{40}H_{48}O_4 \cdot H_2O$, $M = 1124.70\,\mathrm{g\,mol^{-1}}$, monoclinic system, space group $P2_1/n$, $a = 13.0088(1)$, $b = 16.0730(2)$, $c = 21.8701(3)$ Å, $\beta = 101.311(1)$, $Z = 4$, $V = 4484.0(1)\,\text{Å}^3$, $D_c = 1.72\,\mathrm{g\,cm^{-3}}$, μ(Mo–Kα) $= 9.87\,\mathrm{mm^{-1}}$, crystal dimensions of 0.2 × 0.3 × 0.3 mm. 68841 reflections were integrated ($\theta_{max} = 27.48°$). The structure was solved by direct methods [29]. The whole structure was refined anisotropically by full matrix least-squares on F values [30] to final $R = 0.034$ and $Rw = 0.035$ ($\Delta\rho_{max} = 0.69$ and $\Delta\rho_{min} = -1.75\,\mathrm{e}\text{Å}^{-3}$) using 616 parameters for 8035 independent reflections with $I > 1.96\sigma(I)$. Disorder of two propoxy groups was modelled. Carbon atoms with an occupancy in the range 0.05–0.25 were included. Hydrogen atoms were not placed to these atoms. The resting hydrogen atoms were found from a Fourier map and expected geometry. Only positions of fully occupied hydrogen atoms were refined.

X-ray data for **4**: $2AgCF_3SO_3 \cdot C_{32}H_{32}O_4$, $M = 994.48\,\mathrm{g\,mol^{-1}}$, monoclinic system, space group $C2/c$, $a = 18.8110(4)$, $b = 17.8840(3)$, $c = 10.8090(2)$ Å, $\beta = 98.131(1)$, $Z = 4$, $V = 3599.8(1)\,\text{Å}^3$, $D_c = 1.84\,\mathrm{g\,cm^{-3}}$, μ(Mo–Kα) $= 12.92\,\mathrm{mm^{-1}}$, crystal dimensions of 0.2 × 0.2 × 0.3 mm. 27201 reflections were integrated ($\theta_{max} = 27.48°$). The structure was solved by direct methods [29]. The whole structure was refined anisotropically by full matrix least-squares on F values [30] to final $R = 0.041$ and $Rw = 0.040$ ($\Delta\rho_{max} = 0.72$ and $\Delta\rho_{min} = -1.87\,\mathrm{e}\text{Å}^{-3}$) using 345 parameters for 3409 independent reflections with $I > 1.96\sigma(I)$. Disorder of triflate anion was modelled. Hydrogen atoms were found from the expected geometry and were refined isotropically.

Acknowledgements

The authors thank the Grant Agency of the Czech Republic for financial support for this work (GA 104/00/1722 and GA 203/99/M037).

References

[1] *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, 2001.

[2] Gutsche, C. D. In *Calixarenes revisited: Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1998; Vol. 6.

[3] *Calixarenes 50th Anniversary: Commemorative Issue*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic Publishers: Dordrecht, 1994.

[4] *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, 1991.

[5] Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303, and references therein.

[6] Gokel, G. W.; DeWall, S. L.; Meadows, E. S. *Eur. J. Org. Chem.* **2000**, 2967.

[7] Lhoták, P.; Shinkai, S. *J. Phys. Org. Chem.* **1997**, *10*, 273.

[8] Kleina, C.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Chem. Commun.* **2000**, 239.

[9] Orrm, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049.

[10] Sidorov, V.; Kotch, F. W.; El-Kouedi, M.; Davis, J. T. *Chem. Commun.* **2000**, 2369.

[11] Hajek, F.; Graf, E.; Hosseini, M. W.; Delaigue, X.; DeCian, A.; Fischer, J. *Tetrahedron Lett.* **1996**, *37*, 1401.

[12] Castellano, R. K.; Rebek, Jr., J. *J. Am. Chem. Soc.* **1998**, *120*, 3657.

[13] Kim, K. S. *Curr. Appl. Phys.* **2002**, *2*, 65.

[14] Budka, J.; Lhoták, P.; Stibor, I.; Michlová, V.; Sýkora, J.; Cisarová, J. *Tetrahedron Lett.* **2002**, *43*, 2857.

[15] Ning, G. L.; Munakata, M.; Wu, L. P.; Maekawa, M.; Suenaga, Y.; Kuroda-Sowa, T.; Sugimoto, K. *Inorg. Chem.* **1999**, *38*, 5668.

[16] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

[17] Ino, I.; Wu, L. P.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sakai, R. *Inorg. Chem.* **2000**, *39*, 5430.

[18] Ning, G. L.; Wu, L. P.; Sugimoto, K.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2529.

[19] Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. *Inorg. Chem.* **2001**, *40*, 3191.

[20] Wu, L. P.; Dai, J.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ohno, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 3255.

[21] Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K.; Ino, I. *J. Chem. Soc., Dalton Trans.* **1999**, 373.

[22] Matthews, S. E.; Schmitt, P.; Felix, V.; Drew, M. G. B.; Beer, P. D. *J. Am. Chem. Soc.* **2002**, *124*, 1341.

[23] Ikeda, A.; Tsuzuki, H.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2*, **1994**, 2073.

[24] Ikeda, A.; Shinkai, S. *Tetrahedron Lett.* **1992**, *33*, 7385.

[25] Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102.

[26] Lhoták, P.; Nakamura, R.; Shinkai, S. *Supramol. Chem.* **1997**, *8*, 333.

[27] Xu, W.; Puddephatt, R. J.; Muir, K. W.; Torabi, A. A. *Organometallics* **1994**, *13*, 3054.

[28] Hooft, R. W. *COLLECT*; Nonius: Delft, The Netherlands, 1998.

[29] Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

[30] Watkin, D. J.; Prout, C. K.; Carruthers, R. J.; Betteridge, P. *CRYSTALS*; Chemical Crystallography Laboratory: Oxford, UK, 1996, Issue 10.