Polypseudorotaxane architecture of poly-bis[4-(N-benzyl-pyridinium)]piperazine-hexa-thiocyanato-di-cadmium(II) with 2-D honeycomb-like $[Cd(SCN)_3]_n^{n-}$ anionic polymeric framework†

Long-Li Lai,*[a] Chun-Han Wu,[a] Kuang-Lieh Lu,[b] Yu-Shen Wen,[b] Yi-Hung Liu,[c] Yu Wang,[c] Kung-Lung Cheng,[d] Dmitriy V. Soldatov,[e] Zhi Yu[f] and Kui Yu[f]

Received 26th January 2007, Accepted 12th March 2007
First published as an Advance Article on the web 20th March 2007
DOI: 10.1039/b701229b

An unusual, honeycomb-like cadmium-tri-thiocyanate polymeric framework was found in the studied hybrid material of general formula $(L^{2+})_n[Cd(SCN)_3]_{2n}^{2n-}$ (3), where L^{2+} is bis[4-(N-benzylpyridinium)]piperazine dication. The perforated coordination net forms due to a template effect of the organic dications which reside in the holes penetrating the net in a polyrotaxane-like manner. The salt $(L^{2+})(SCN)_2\cdot 2H_2O$ (4) was studied for comparison.

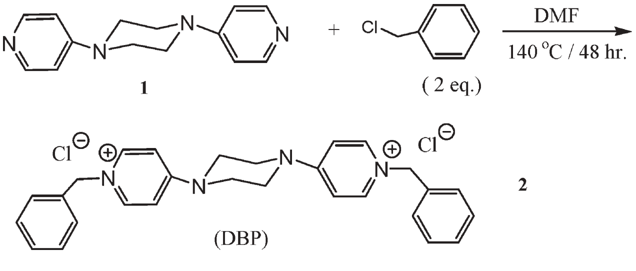
Supramolecular self-assembly of pre-selected reactants is an important approach for generating new chemical entities, from simple discrete species to polymeric frameworks,[1] and unusual species may be created while using certain combinations of participating components.[2] Organic–inorganic hybrid materials well illustrate this approach presenting new fascinating inorganic structures resulting from the interaction "with organic component". The components used in our studies, cadmium(II), thiocyanate anion and dipyridinium-based organic cation, may create a set of important properties when combined in a supramolecular solid. The dipyridinium cations and their derivatives are of considerable interest due to their specific physical properties and potential applications in biology and photochemistry.[3] On the other hand, the Cd–N complexes exhibited such qualities as nonlinear optical (NLO) property[4] and ligand-to-metal charge-transfer (LMCT) in the solid state.[5]

Previous studies on hybrid architectures with dipyridinium-type cations were concentrated on the variation of the metal complex to construct 1-D or 2-D inorganic frameworks, such as $Cd_m(SCN)_n^{x-}$, $Cd_3(CN)_6Cl^{2-}$, PbI_3^{1-} or $V_2O_5^{0.5-}$, as "the inorganic complexes" are very versatile for the designing purpose. However, none of these architectures have ever been found to possess a rotaxane-like topology.[4,6] In contrast to the previous studies, our efforts were concentrated on the organic dipyridinium cation and its potential to act as a template in self-assembly of Cd-SCN polymeric nets.[6a] It was believed that the geometry of the organic cation as well as its propensity for the formation of hydrogen bonds with inorganic component may affect the assembly of the inorganic net, with the resulting structural anisotropy being a basis for potential applications of the materials in the optical area. This communication reports the synthesis and X-ray crystallographic study of a novel hybrid architecture in which the organic dipyridinium cation penetrates the inorganic cadmium-tri-thiocyanate network.

Scheme 1 elucidates the preparation method and structural formula of the designed template. Bis(4-pyridyl)piperazine **1**[7] was used to prepare the target bis[4-(N-benzylpyridinium)]piperazine dication **2** as the dichloride salt $(\mathbf{2})Cl_2\cdot 3H_2O$. Compound **3**, with stoichiometry $(\mathbf{2})Cd_2(SCN)_6$, was prepared as a yellow crystalline product.

The crystal structure determination of compound **3** revealed its hybrid nature and supramolecular organization as shown in Fig. 1 and 2. The compound is described by the formula $(\mathbf{2})_n[Cd(SCN)_3]_{2n}$ which reflects the presence of two components in the structure: organic dications **2** and a cadmium thiocyanate anionic network, with no chemical bonds connecting the components in the crystal. There is a sandwich-like stacking of alternating inorganic and organic layers propagating in *b* and *c* directions of the crystal while the layers alternate along the *a*-axis (Fig. 1). The packing of the layers is controlled by van der Waals forces; no π–π or hydrogen bonding interactions were found within the organic layer.

The inorganic layer has the stoichiometry $[Cd(SCN)_3]^-$ and a coordination polymeric structure. The Cd(II) cation is coordinated by three N and three S atoms of six SCN^--groups. At the same time, each SCN^--group bridges two Cd(II) cations. This mode of coordination produces a distorted honeycomb 2-D network with



Scheme 1 Preparation of dication **2** as a dichloride salt

---

[a] *Department of Applied Chemistry, National Chi Nan University, Puli, Taiwan 545 E-mail: lilai@ncnu.edu.tw*
[b] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115*
[c] *Instrumentation Center and Department of Chemistry, National Taiwan University, Taipei, Taiwan 106*
[d] *Applied Chemistry Division, Material and Chemical Research Laboratories, Industrial Research Institute, Hsinchu, Taiwan 300*
[e] *Institute of Inorganic Chemistry, Siberian Division of the Russian Academy of Sciences, Acad. Nikolaev Av. 3, Novosibirsk 630090, Russian Federation*
[f] *Steacie Institute for Molecular Sciences, National Research Council Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6*

† Electronic supplementary information (ESI) available: TGA of complexes **3** and **4** under nitrogen; ORTEP of hybrid **3** and compound **4** with 50% probability thermal ellipsoids. See DOI: 10.1039/b701229b

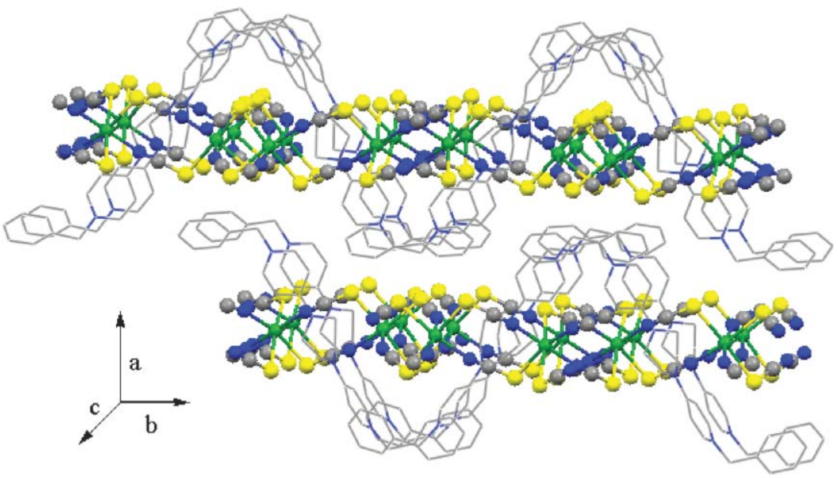


Fig. 1 Molecular packing in hybrid **3**. Inorganic network is shown in ball-and-stick style and organic cations are shown in wire style (C, gray; N, blue; S, yellow; Cd, green; H atoms are omitted).

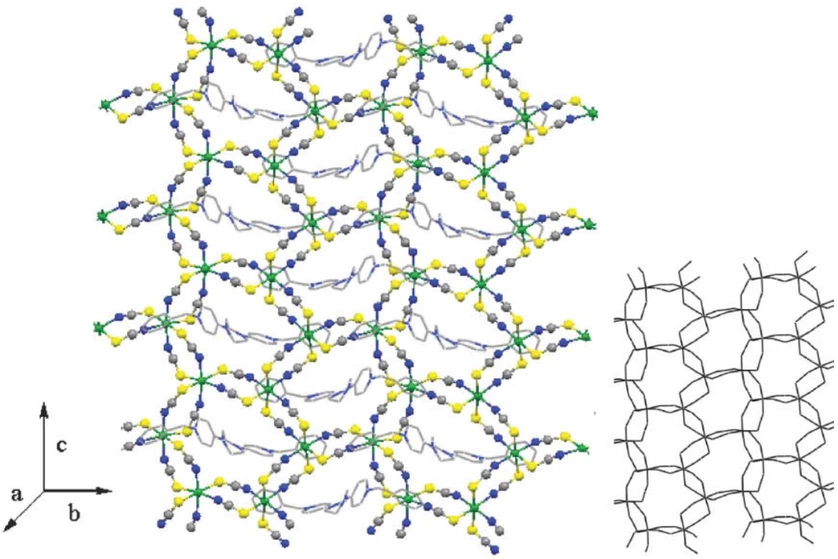


Fig. 2 View of part of the hybrid structure **3** along *a* axis. Left: inorganic network is shown in ball-and-stick style and organic cations are shown in wire style. Right: inorganic network is shown in wire style and organic cations are omitted

Cd atoms in the vertices and pairs of SCN-bridges connecting them (Fig. 2). The network is negatively charged, with (2−) charge per each $Cd_6(SCN)_{12}$ ring. Further, each ring is penetrated by the organic dication **2** so that the central part of the dication resides inside the ring while its hydrophobic ends contribute to the formation of the hydrophobic layers on both sides of the inorganic net. Topologically, this architecture may be described as a polypseudorotaxane.

Simple rotaxane is formed by two mechanically interlocked molecules, "the axle molecule" threaded into "the wheel molecule".[8,9] Polyrotaxanes have attracted significant attention recently in the area of organic synthesis, the species resulting from the combination of a large number of wheels and a polymeric axle molecule threaded through them ("molecular necklaces").[10] Poly(ethylene glycol) and other organic molecules were used as the axle component, with cyclodextrins,[11] crown ethers,[12] cucurbiturils and other macrocycles[13] utilized as wheels. Polyrotaxanes with coordination polymers of various dimensionalities and cyclodextrins,[14] crown ethers,[15] cucurbiturils[16] as wheels also have been reported. Other examples with metal complexes included parallel 1-D coordination polymers with an infinite sequence of rings penetrated in another direction with 1-D polymeric axles[17] and similar grids formed by 1-D coordination polymers consisting of alternating axle and wheel segments.[18] There was one example reported "where 1-D polymeric chains penetrated 2-D coordination polymeric net".[19] At the same time, the polyrotaxane architecture observed in our study and consisting of a 2-D inorganic network perforated with organic molecules has never been reported before and deserves special consideration.

The structure of the $[Cd(SCN)_3]_n^{n-}$ polymeric network is particularly interesting. A great number of cadmium thiocyanate complexes have been studied and many of them contain the Cd–SCN–Cd link and eight-membered ring as observed in the title structure. When Cd(II) forms four links participating in two

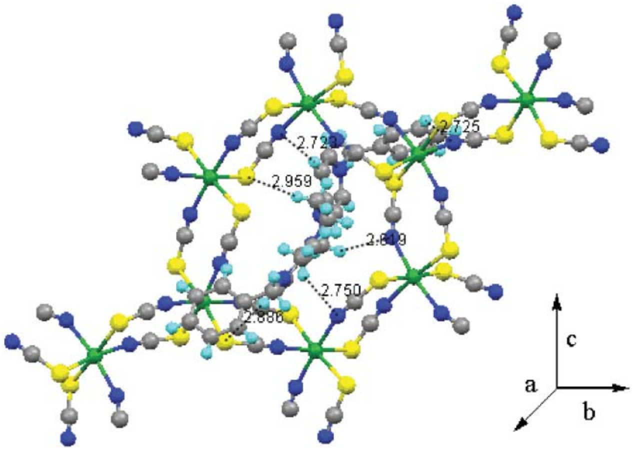


Fig. 3 H-bonds between organic and inorganic moieties in hybrid **3**.

adjacent eight-membered rings, either 1-D polymeric chains as $[Cd(SCN)_2Q_2]_n$ with the residual two axial coordination sites occupied by terminal ligands Q are formed,[20] or 2-D polymeric sheets develop if a bridging ligand is used instead.[21] When Cd(II) forms six links, each of them connects another Cd(II), and 1-D anionic chains are formed[22] with the same formula, $[Cd(SCN)_3]_n^{n-}$, as the 2-D net observed in the title compound. The 3-D networks based on cadmium thiocyanate have been reported in the literature, requiring the use of additional ligands.[23] Finally, 1-D chains were also observed in cadmium thiocyanate complex,[24] where each Cd(II) is linked to two adjacent Cd(II) centers by four SCN^- bridges in the equatorial plane, while the axial coordination sites are occupied by S atoms from neighboring chains. In comparison with the known cadmium thiocyanate polymers, the honeycomb-like network observed in the title compound is very unusual and can hardly form unless a suitable templating agent is present in the reaction mixture.

The ability of the dipyridinium cation **2** to template the formation of the observed type of inorganic polymeric network is likely to be a result of three factors. First, the charge on the dication is partially delocalized towards the middle part of the molecule and the penetration appears to be a suitable way to compensate the charge of the anionic net. Second, the geometry of the middle part of the dication (piperazine fragment) provides a good fit to the hole in the eight-membered $Cd_6(SCN)_{12}$ ring. Finally, there seem to be weak noncovalent interactions between the components (Fig. 3). The N···H and S···H distances vary within 2.62–2.75 and 2.87–2.96 Å, respectively, implying weak $C–H\cdots N_{CS}$ and $C–H\cdots S_{CN}$ bonds.[25]

For the purpose of comparison, the thiocyanate salt of **2** was isolated and studied. The crystal structure of the salt conforms with the formula $(\mathbf{2})(SCN)_2\cdot 2H_2O$ (hereinafter **4**); the packing diagram is shown in Fig. 4. As in the previous structure, there are well distinguished organic and inorganic layer fragments alternating along the *a*-axis. Also, in addition to strong hydrogen bonds formed by water, there are similar weak hydrogen bonds as in **3** (Fig. 5). The comparison of the piperazine fragments in the crystals of **3** and **4** indicates that the piperazine ring in **4** adopts a regular chair conformation while in **3** it is in a distorted boat form [both C–N–C angles in hybrid **4** are 111.5(4)° while in **3** they are 115.1(1) and 115.4(1)°]. Therefore, the organic dication displays an ability to adjust its geometry in order to satisfy packing requirements and to facilitate noncovalent interactions present in the crystalline solids.

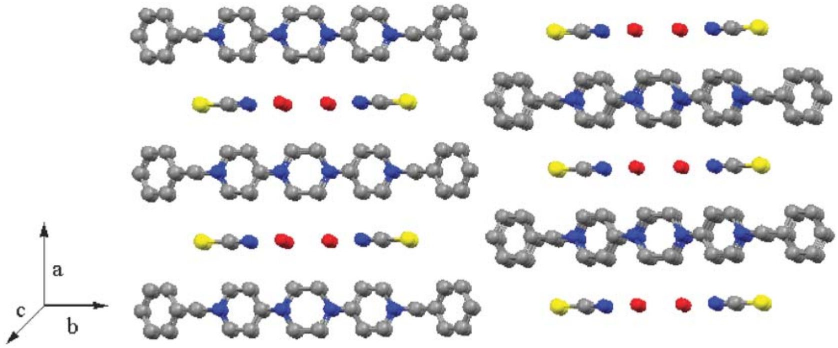


Fig. 4 The crystal packing in salt **4** (C, gray; N, blue; O, red; S, yellow; H atoms are omitted)

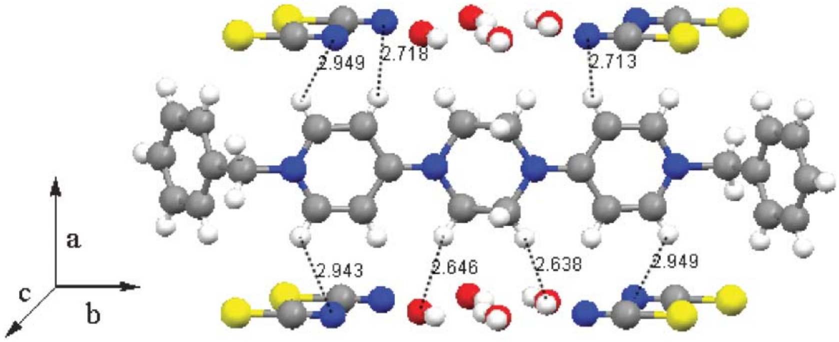


Fig. 5 H-bonds in salt **4**

In order to compare the contribution of the organic dication to overall stability of the crystalline **3** and **4**, the bulk materials were examined with TGA. Compound **3**, $(\mathbf{2})_n[\mathrm{Cd(SCN)_3}]_{2n}$, decomposes in a single step, with the mass loss of 54% being in good agreement with 54.1% calculated for the release of $(\mathbf{2})(\mathrm{SCN})_2$ salt (as volatile products) to yield polymeric cadmium thiocyanate $[\mathrm{Cd(SCN)_2}]_n$. The onset temperature of this process is 299 °C. In contrast, the decomposition of unhydrated **4**, $(\mathbf{2})(\mathrm{SCN})_2$, starts at 263 °C. Therefore, the 2-D inorganic framework in **3**, to some extent, stabilizes the hybrid system, although the torsional strength from piperazine moiety in **3** is greater than that in **4**. This observation provides a new example of contact stabilization and self-stabilization phenomena.[2,26]

In summary, a novel hybrid architecture was prepared from bis[4-(N-benzylpyridinium)]piperazine and cadmium(II) thiocyanates, in which an unusual, honeycomb-like 2-D cadmium-tri-thiocyanate anionic network is penetrated by the dipyridinium cations to form a polypseudorotaxane structure. To our best knowledge, this is the first example showing such an interesting geometry in the organic–inorganic hybrids. It should be noted that the new template **2** has a great potential for further functionalization. For example, functional groups may be attached to the terminal phenyl rings for a specifically desired property or other alkyl moiety instead of piperazine can be used to connect two pyridine rings to adjust the solubility or conformation of the organic template.[27] The synthesis and utilization of such modified organic templates is a subject of our future studies.

This work was financially supported by the National Chi Nan University and the National Science Council (NSC 94-2113-M-260-004).

Preparation of $(\mathbf{2})\mathrm{Cl_2}\cdot3\mathrm{H_2O}$

Bis(4-pyridyl)piperazine **1**, prepared according to a literature procedure,[7] was treated with two equivalents of benzyl chloride in DMF (10 ml) at 140 °C for two days to give bis[4-(N-benzylpyridinium)]piperazine dichloride trihydrate $(\mathbf{2})\mathrm{Cl_2}\cdot3\mathrm{H_2O}$ in 81% yield (see Scheme 1). ^{1}H-NMR, δ ($\mathrm{CDCl_3}$): 3.89 (8H, s, 4 × $\mathrm{CH_2}$ of piperazine), 5.43 (4H, s, 2 × $\mathrm{CH_2}$ of benzyl), 7.21 (4H, d, *J* = 7.2 Hz, 4 × Ar–H of pyridine), 7.36 (10H, s, 10 × Ar–H of benzyl), 8.50 (4H, d, *J* = 7.2 Hz, 4 × Ar–H of pyridine). Calculated for $\mathrm{C_{28}H_{30}Cl_2N_4} + 3\mathrm{H_2O}$ (%): C, 61.42; H, 6.63; N, 10.23. Found (%): C, 61.57; H, 6.57; N, 10.33.

Preparation of $(\mathbf{2})_n[\mathrm{Cd(SCN)_3}]_{2n}$ (3)

$\mathrm{Cd(NO_3)_2}$ (0.0473 g, 0.20 mmol) and KSCN (0.0970 g, 1.00 mmol) were mixed in methanol (10 ml), and the solid $\mathrm{KNO_3}$ was filtered and discarded. Salt **2** (0.05 g, 0.10 mmol) was dissolved in water (15 ml) and added to the filtrate. The resulting solution was allowed to stand at room temperature for two weeks. Pale yellow crystals **3** formed from the solution were separated by filtration, washed with dried ethyl acetate and air-dried to give 0.021 g (yield 20%). Calculated for $\mathrm{C_{34}H_{30}Cd_2N_{10}S_6}$ (%): C, 41.01; H, 3.25; N, 14.07. Found (%): C, 41.15; H, 3.17; N, 13.93.

Preparation of $(\mathbf{2})(\mathrm{SCN})_2\cdot2\mathrm{H_2O}$ (4)

KSCN (0.0970 g, 1.00 mmol) and salt $(\mathbf{2})\mathrm{Cl_2}\cdot3\mathrm{H_2O}$ (0.05 g, 0.10 mmol) were dissolved in water (10 ml), and the resulting solution was allowed to stand at room temperature for a week. Colorless crystals **4**, formed from the solution were separated by filtration, washed with dried ethyl acetate and air-dried to give 0.029 g (yield 49%). Calculated for $\mathrm{C_{30}H_{30}N_6S_2} + 2\mathrm{H_2O}$ (%): C, 62.69; H, 5.96; N, 14.62. Found (%): C, 62.50; H, 5.96; N, 14.58.

X-Ray crystallography

Single crystals of **3** and **4** were studied on a CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) at 100 and 295 K, respectively. The structures were solved using SHELXS-97 program and refined using SHELXL-97 anisotropically for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and were refined isotropically (except for the hydrogen atoms of water molecules in **4**). Crystal data and selected refinement details are listed below, while full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or by request from the following electronic address: deposit@ccdc.cam.ac.uk. CCDC reference numbers 288698 and 628691. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701229b

Crystal data for **3** (T = 100 K): $\mathrm{C_{34}H_{30}Cd_2N_{10}S_6}$, M = 995.84, monoclinic, space group $P2_1/c$, a = 20.8688(6), b = 18.5411(5), c = 9.8944(3) Å, β = 94.905(1)°, V = 3814.4(2) Å^3, Z = 4, d = 1.734 cm^3 g^{-1}, $R1$ = 0.017, $wR1$ = 0.042 with goodness-of-fit on F^2 = 1.139. CCDC No: 288698. Crystal data for **4** (T = 295 K): $\mathrm{C_{30}H_{34}N_6O_2S_2}$, M = 574.75, orthorhombic, space group $Pnnm$, a = 41.046(4), b = 4.5649(5), c = 7.9777(8) Å, V = 1494.8(8) Å^3, Z = 2, d = 1.277 cm^3 g^{-1}, $R1$ = 0.076, $wR1$ = 0.207 with goodness-of-fit on F^2 = 1.115. CCDC No: 628691.

Notes and references

1 (*a*) J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*b*) A. D. Hamilton, *Perspectives in Supramolecular Chemistry*, Wiley, New York, 1996.

2 (*a*) D. V. Soldatov and J. A. Ripmeester, *Supramolecular Stabilization*, in Encyclopedia of Supramolecular Chemistry, ed. J. L. Atwood and J. W. Steed, Marcel Dekker, New York, 2004, 1453; (*b*) D. V. Soldatov, *J. Inclusion Phenom.*, 2004, **48**, 3.

3 (*a*) C. A. Schalley, C. Verhaelen, F.-G. Klarner, U. Hahn and F. Vogtle, *Angew. Chem., Int. Ed.*, 2005, **44**, 477; (*b*) W. Ong, J. Grindstaff, D. Sobransingh, R. Toba, J. M. Quintela, C. Peinador and A. E. Kaifer, *J. Am. Chem. Soc.*, 2005, **127**, 3353; (*c*) M. Grätzel, *Heterogeneous Photochemical Electron Transfer*, Wolfe, London, 1988; (*d*) *Photochemical Energy Conversion*, ed. J. R. Norris and D. Meisel, Elsevier, New York, 1989.

4 H. Zhang, X. Wang, K. Zhang and B. K. Toe, *Coord. Chem. Rev.*, 1999, **183**, 157 and references therein.

5 (*a*) B.-C. Tzeng, Y.-M. Lu, G.-H. Lee and S.-M. Peng, *Eur. J. Inorg. Chem.*, 2006, 1698; (*b*) L.-Y. Zhang, G.-F. Liu, S.-L. Zheng, B. H. Ye, X.-M. Zhang and X.-M. Chen, *Eur. J. Inorg. Chem.*, 2003, 2965; (*c*) J.-H. Luo, M.-C. Hong, R.-H. Wang, R. Cao, L. Han and Z.-Z. Lin, *Eur. J. Inorg. Chem.*, 2003, 2705.

6 (*a*) Z. Yu, K. Yu, L. L. Lai, K. A. Udachin, H. Zhu, J. Tao, X. You, M. Ströbele, H.-J. Meyer and J. A. Ripmeester, *Chem. Commun.*, 2004, 648; (*b*) Z. J. Tang and A. Guloy, *J. Am. Chem. Soc.*, 1999, **121**, 452; (*c*) H. Yoshikawa, S. Nishikiori, K. Suwinska, R. Luboradzki and J. Lipkowski, *Chem. Commun.*, 2001, 1398; (*d*) A. Bose, P. He, C. Liu, B. D. Ellman, R. J. Twieg and S. P. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 4.

7 R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1625.

8 (*a*) P. Linnartz and C. A. Schalley, *Rotaxanes and Pseudorotaxanes*, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker, New York, 2004, 1194; (*b*) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971.

9 In a true rotaxane the axle is restrained to remain inside the wheel due to bulky ending groups, while in a pseudorotaxane the restriction occurs due to noncovalent forces between the two molecules.

10 F. Huang and H. W. Gibson, *Prog. Polym. Sci.*, 2005, **30**, 982.

11 (*a*) G. Fleury, C. Brochon, G. Schlatter, G. Bonnet, A. Lapp and G. Hadziioannou, *Soft Matter*, 2005, **1**, 378; (*b*) P. A. Kalashnikov, V. I. Sokolov and I. N. Topchieva, *Russ. Chem. Bull.*, 2005, **54**, 1973; (*c*) J. Araki and K. Ito, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6312; (*d*) J. H. Son, Y. S. Kang and J. Won, *J. Membr. Sci.*, 2006, **281**, 345.

12 (*a*) C. Gong and H. W. Gibson, *Curr. Opin. Solid State Mater. Sci.*, 1997, **2**, 647; (*b*) H. W. Gibson and P. T. Engen, *Polymer*, 1999, **40**, 1823.

13 T. Takata, N. Kihara and Y. Furusho, *Adv. Polym. Sci.*, 2004, **171**, 1.

14 (*a*) Y.-W. Yang, Y. Chen and Y. Liu, *Inorg. Chem.*, 2006, **45**, 3014; (*b*) Y.-L. Zhao, H.-Y. Zhang, D.-S. Guo and Y. Liu, *Chem. Mater.*, 2006, **18**, 4423.

15 (*a*) G. J. E. Davidson and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2003, **42**, 74; (*b*) S. J. Loeb, *Chem. Commun.*, 2005, 1511.

16 (*a*) J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte, *Ind. Eng. Chem. Res.*, 2000, **39**, 3419; (*b*) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96; (*c*) K.-M. Park, E. Lee, S.-G. Roh, J. Kim and K. Kim, *Bull. Korean Chem. Soc.*, 2004, **25**, 1711.

17 (*a*) M. J. Plater, M. R. S. J. Foreman, T. Gelbrich and M. B. Hursthouse, *Cryst. Eng.*, 2001, **4**, 319; (*b*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.

18 (*a*) L. Carlucci, G. Ciani and D. M. Proserpio, *Cryst. Growth Des.*, 2005, **5**, 37; (*b*) K. Kasai and M. Sato, *Chem.–Asian J.*, 2006, **1**, 344.

19 M.-L. Tong, Y.-M. Wu, J. Ru, X.-M. Chen, H.-C. Chang and S. Kitagawa, *Inorg. Chem.*, 2002, **41**, 4846.

20 (*a*) M. Taniguchi, M. Shimoi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2299; (*b*) D. Bose, J. Banerjee, S. H. Rahaman, G. Mostafa, H.-K. Fun, R. D. B. Walsh, M. J. Zaworotko and B. K. Ghosh, *Polyhedron*, 2004, **23**, 2045; (*c*) D. Vujovic, H. G. Raubenheimer and L. R. Nassimbeni, *Eur. J. Inorg. Chem.*, 2004, 2943; (*d*) S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak and A. Ghosh, *Inorg. Chim. Acta*, 2005, **358**, 535.

21 J. Luo, M. Hong, R. Wang, R. Cao, Q. Shi and J. Weng, *Eur. J. Inorg. Chem.*, 2003, 1778.

22 (*a*) W. Chen, F. Liu and X. You, *J. Solid State Chem.*, 2002, **167**, 119; (*b*) F. Liu, W. Chen and X. You, *J. Solid State Chem.*, 2002, **169**, 199; (*c*) S. Sain, T. K. Maji, G. Mostafa, T.-H. Lu and N. R. Chaudhuri, *J. Coord. Chem.*, 2003, **56**, 1157; (*d*) X.-J. Feng, J.-X. Yang, W.-T. Yu, H.-K. Fun, J.-Y. Wu and Y.-P. Tian, *Chin. J. Inorg. Chem.*, 2004, **20**, 403.

23 (*a*) A. Mondal, G. Mostafa, A. Ghosh, I. R. Laskar and N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 1999, 9; (*b*) G. Mostafa, A. Mondal, I. R. Laskar, A. J. Welch and N. R. Chaudhuri, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 146; (*c*) M. A. S. Goher, F. A. Mautner, A. K. Hafez, M. A. M. Abu-Youssef, C. Gspan and A. M.-A. Badr, *Polyhedron*, 2003, **22**, 975.

24 M. Cannas, G. Carta, A. Cristini and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 1976, 300.

25 (*a*) F. H. Allen, J. M. P. Lommerse, V. J. Hoy, J. A. K. Howard and G. R. Desiraju, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1996, **52**, 734; (*b*) G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565.

26 (*a*) T. Iwamoto, S. Nishikiori, Y. A. Dyadin and D. V. Soldatov, *J. Struct. Chem.*, 1999, **40**, 750; (*b*) E. A. Ukraintseva and D. V. Soldatov, *J. Struct. Chem.*, 2005, **46**, S175.

27 Q.-Y. liu and L. Xu, *CrystEngComm*, 2005, **7**, 87.