



Synthesis of Carboxymethyl Calix[4]arene Intercalated Layered Double Hydroxides

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The intercalation of water-soluble carboxymethyl calix[4]arene (CMCS) in the interlayer of the Zn-Al layered double hydroxides powder and film by the anion exchange and *in situ* crystallization methods have been investigated. The XRD results confirm the intercalation of carboxymethyl calix[4]arene in the interlayer galleries of layered double hydroxides. In both powder and film samples, carboxymethyl calix[4]arene molecules adopt a monolayer arrangement, with the axis of the cavity perpendicular to the layered double hydroxides sheets. The SEM images indicate that the *ab-face* of layered double hydroxides microcrystals is predominantly perpendicular with respect to the porous anodic alumina substrate. Compared with the CMCS-LDHs powder sample, the structured CMCS-LDHs film exhibits the advantages of more convenient operation. This carboxymethyl calix[4]arene functionalized inorganic layered film may have potential application in the field of industrial adsorption, separation and inclusion.

Key Words: Layered double hydroxides, Calix[4]arene, *In situ* crystallization, Film.

INTRODUCTION

Layered double hydroxides (LDHs) are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and solvation molecules. In the layered double hydroxides layers, the metal cations occupy the centers of edge sharing octahedra, whose vertexes contain hydroxide ions that connect to form infinite 2D sheets. Layered double hydroxides can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} , Ca^{2+} , Mn^{2+} , Cu^{2+} and Al^{3+} , Ga^{3+} , respectively, A^{n-} is an anion, such as CO_3^{2-} , SO_4^{2-} , or NO_3^{-1-5} . Layered double hydroxides have recently received increasing attention, owing to their versatility and usefulness in a wide range of technological applications such as catalysis⁶, functional materials⁷, two-dimensional solid-state nanoreactors⁸, bioactive nanocomposites⁹, etc.

In the commonly observed powder form, layered double hydroxides have a house-of-cards structure involving edge-to-face particle interactions, which limits their research and application. The most effective solution to this problem may be preparation of layered double hydroxides film on substrates. Pinnavaia *et al.*¹⁰ found that the colloidal layered double hydroxides suspensions obtained by hydrolysis of alkoxide intercalated layered double hydroxides derivatives were able

to form transparent film. Li *et al.*¹¹ were the first to assemble Mg-Al layered double hydroxides nanosheets by layer-by-layer methods with an anionic polymer, poly(sodium styrene 4-sulfonate) (PSS), onto the solid surface to produce ultrathin nanocomposite films¹¹. In the recent years, there have been rising research interests in the fabrication of thin films from layered double hydroxides nanosheets by the layer-by-layer method and such fabricated thin films have been used in many fields such as luminescence^{12,13}, electrocatalysis^{14,15}, fluorescence chemosensors¹⁶, bioanalysis and biodetection¹⁷, antireflection coatings¹⁸ and inorganic sandwich-layered materials^{19,20}. Our group has recently reported fabrication of CMCD-LDHs film with the *c*-axis parallel to the substrate, by means of employing porous anodic alumina/aluminum as both substrate and sole source of aluminum. Furthermore, this film can be used to enantioselectively separate racemic molecules, 1-phenyl-1,2-ethanediol (PED) and included fullerene by the CMCD on the surface of layered double hydroxides^{21,22}.

Calixarenes are macrocyclic molecules of the metacyclophanes, consisting of several phenol units (usually four to eight) connected *via* methylene bridges in the *ortho* position with respect to the hydroxyl group²³⁻²⁵. The word calixarene is derived from calix or chalice because this type of molecule resembles a vase and from the word arene that refers to the aromatic building block. They are characterized by a three-dimensional basket, cup or bucket shape²⁶⁻²⁸. In calix[4]arenes, the internal volume is around 10 cubic nanometers. Calixarenes

have a hydrophobic cavity that can hold smaller molecules or ions and belong to the class of cavitands known in host-guest chemistry. Moreover, calixarene host molecules have a unique composition that includes benzene groups, which provide π - π interaction and hydroxyl groups for hydrogen bonding. The calixarene cavity is capable of molecular recognition in solution^{29,30}, which is of great interest for application in the remediation of contaminated groundwater and industrial effluents. Calixarenes are also used in commercial applications as sodium selective electrodes for the measurement of sodium levels in blood. Recently, it was found that the calixarene can be used to form complexes with cadmium, lead, lanthanides, actinides and include the C₆₀ and C₇₀ fullerene to form a ball-and-socket supramolecular complex^{31,32}.

In this study, the intercalation of water-soluble 25,26,27,28-tetrakis(Carboxymethyl) calix[4]arene (CMCS) in the interlayer of the Zn-Al layered double hydroxides powder and film (CMCS-LDHs powder and CMCS-LDHs film) by the methods of anion-exchange and *in situ* crystallization on a porous anodic alumina/aluminum (PAO/Al) substrate have been investigated. The CMCS-LDHs nanocrystals can be conveniently used for manipulation as structured adsorbents and molecules container. Furthermore, in the film, the *ab-face* of CMCS-LDHs microcrystals is perpendicular to the substrate and the edges of layered double hydroxides plates are exposed to the outside, which is more favourable to adsorb solute or inclusion molecules from outside solution.

EXPERIMENTAL

All chemicals including Zn(NO₃)₂·6H₂O, NH₄NO₃, NH₃·H₂O, chloroacetic acid, calix[4]arenes were of analytical grade. They were purchased from the Beijing Chemical Plant Limited. Aluminum metal sheet was purchased from Shanghai Jing Xi Chemical Technology Co. Ltd., purity: >99.5 %, thickness: 0.1 mm.

Synthesis of 25,26,27,28-tetrakis(carboxymethyl) calix[4]arene (CMCS): CMCS was synthesized according to the procedure described in the literature³³ with some modifications. To a refluxing suspension of calix[4]arene (3.00 g, 6.80 mmol) and Cs₂CO₃ (13.3 g, 40.5 mmol) in dry acetone (220 mL) was added dropwise a solution of chloroacetic acid (5.13 g, 54.3 mmol) in dry acetone (70 mL) over 3 h under nitrogen atmosphere. The reaction mixture was refluxed for an additional 30 h. After cooling of the reaction to room temperature, the salt was filtered off and the solvent was removed *in vacuo*. The reaction mixture was extracted three times with 100 mL of CH₂Cl₂, washed twice with water and dried over anhydrous MgSO₄ and then the solvent was removed *in vacuo*. The crude product was chromatographed on silica gel using a mixture of ethyl acetate and *n*-hexane (1:5) as an eluent. Recrystallization from CH₂Cl₂/*n*-hexane (1:30, v/v) gave a white crystalline solid in 18.3 % yield (0.752 g).

Synthesis of CMCS-LDHs powder: The precursor NO₃-LDHs was prepared by a coprecipitation method similar to that reported previously^{34,35}. A solution of Zn(NO₃)₂ (0.12 mol) and Al(NO₃)₃ (0.06 mol) in deionized water (200 mL) was added dropwise over 2 h to a solution of NaOH (0.31 mol)

and NaNO₃ (0.21 mol) in water (100 mL). The white precipitate was obtained collected by centrifugation, washed thoroughly and stored to be used later in an anion-exchange reaction. CMCS-LDHs was obtained by the method of ion exchange^{36,37}. A solution of CMCS (2.5 g) in deionized water (50 mL) was added to a suspension of NO₃-LDHs (10.0 g) in water (100 mL) and the pH of the solution was kept at 6 by adding 0.1 mol/L NaOH solution or 0.1 mol/L HNO₃ solution during the reaction. The mixture was heated at 60 °C under a nitrogen atmosphere for 48 h. The solid was washed thoroughly with deionized water, centrifuged and dried at 70 °C for 20 h. This product is CMCS-LDHs powder.

Synthesis of CMCS-LDHs film: The CMCS-LDHs film was prepared by *in situ* crystallization³⁸ on a porous anodic alumina/aluminum (PAO/Al) substrate. The porous anodic alumina film was fabricated by anodizing an aluminum metal sheet for 1 h in a thermostatic bath of 1 M H₂SO₄ at a temperature of 25 °C and with a current density of 20 mA cm⁻². In this experiment, PAO/Al was used as both the substrate and the sole source of aluminum. In a typical procedure, 0.01 mol of Zn(NO₃)₂·6H₂O, 0.06 mol of NH₄NO₃ and 0.002 mol of CMCS were dissolved in deionized water to form a clear solution with a total volume of 100 mL and the pH was adjusted to 6.5 by adding diluted ammonia (1 % NH₄OH). The PAO/Al substrate was then placed vertically in the solution at 70 °C for 48 h, to obtain the CMCS-LDHs microcrystals grown on the surface of the substrate. Finally, the substrate was taken out, rinsed with water and dried at room temperature. Based on the difference between the initial and final mass of the substrate, the weight of CMCS-LDHs film per unit area of the substrate was calculated to be 3.12 × 10⁻² kg/m².

Characterization of the CMCS-LDHs powder and film: Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). The operating voltage and current were 40 kV and 30 mA, respectively. The step used was 0.02° s⁻¹ in the 2 θ range from 2 to 70°. The morphology of the CMCS-LDHs film was investigated by using a scanning electron microscope with an EDX attachment (SEM: Hitachi S-4700, EDX: Genesis 60). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vector22 spectrophotometer in the range 4000-400 cm⁻¹ with 2 cm⁻¹ resolution. The standard KBr disk method (1 mg of sample in 100 mg of KBr) was used. Metal analysis was performed by inductively coupled plasma (ICP) emission spectroscopy on a Shimadzu ICPS-7500 instrument using solutions prepared by dissolving the samples in dilute HCl. Carbon, hydrogen and nitrogen analyses were carried out using an Elementarvario elemental analysis instrument.

RESULTS AND DISCUSSION

The chemical compositions of the CMCS-LDHs are indicated in Table-1. The metal ratio of all the CMCS-LDHs powder agreed with the mixed ratio (Zn²⁺/Al³⁺ = 2:1). On the other hand, the metal ratio of the CMCS-LDHs film is obviously lower than 2:1, which can be explained by the Al₂O₃ scrapped from the porous anodic alumina/aluminum (PAO/Al) substrate.

TABLE-1
CHEMICAL COMPOSITION OF THE CMCS-LDHs

	Chemical formula	Zn/Al
CMCS-LDHs Powder	$[(Zn^{2+})_{0.67}(Al^{3+})_{0.33}(OH)_2]^{0.33+} \cdot (CMCS^4)_{0.0825} \cdot 3H_2O$	2.03
CMCS-LDHs Film	$[(Zn^{2+})_{0.61}(Al^{3+})_{0.39}(OH)_2]^{0.39+} \cdot (CMCS^4)_{0.0975} \cdot 3H_2O$	1.56

X-ray diffraction of CMCS-LDHs film: The CMCS intercalated layered double hydroxides was synthesized as described in the experimental part. Fig. 1 illustrates the XRD patterns of the PAO/Al substrate, the CMCS-LDHs film as well as the CMCS-LDHs powder and the lattice parameters are listed in Table-2. The sequence of (003), (006) reflections at low angle and the (012) reflection at high angle for the powder and film (Fig. 1b and 1c) indicates formation of well-crystallized hydrotalcite-like layered double hydroxides phase. The reflection can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of layered double hydroxides structures. The interlayer distance of CMCS-LDHs powder and film is 1.817 and 1.844 nm, which are larger than that of NO_3^- -LDHs³⁶. These results confirm the intercalation of CMCS in the interlayer galleries of layered double hydroxides. Moreover, The interlayer distance of CMCS-LDHs are slightly larger than that of the *p*-sulfonated calix[4]arene intercalated layered double hydroxides³⁹. The reason for this is that the CMCS molecule is longer than *p*-sulfonated calix[4]arene. Since the thickness of the layered double hydroxides hydroxide basal layer is 0.480 nm, the gallery height is 1.337 and 1.364 nm. CMCS are characterized by a three-dimensional basket shape, which has an approximate torus thickness of 0.731 nm. Taking into account the dimensions of 25,26,27,28-Tetrakis (carboxymethyl) calix[4]arene molecule and the rule of charge balance, the CMCS anions can only adopt a monolayer arrangement with their cavities axis perpendicular to the layered double hydroxides layer and carboxymethyl groups on adjacent CMCS molecules attached alternately to the upper and lower layered double hydroxides layer surfaces (Fig. 2).

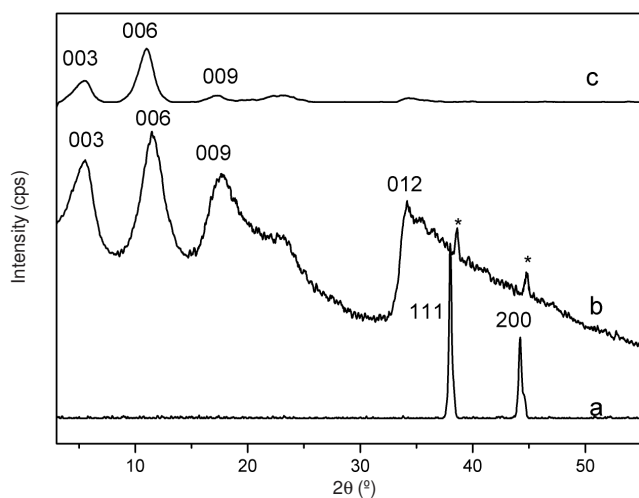


Fig. 1. XRD patterns of (a) the PAO/Al substrate, (b) the CMCS-LDHs film, (c) the CMCS-LDHs powder. Asterisk denotes the reflections of Al substrate

TABLE-2
LATTICE PARAMETERS OF THE CMCS-LDHs POWDER AND THE CMCS-LDHs FILM

Lattice Parameter (nm)	CMCS-LDHs powder	CMCS-LDHs film
d_{003}	1.817	1.844
d_{006}	0.880	0.918
d_{009}	0.594	0.601
Lattice parameter <i>c</i>	5.451	5.532

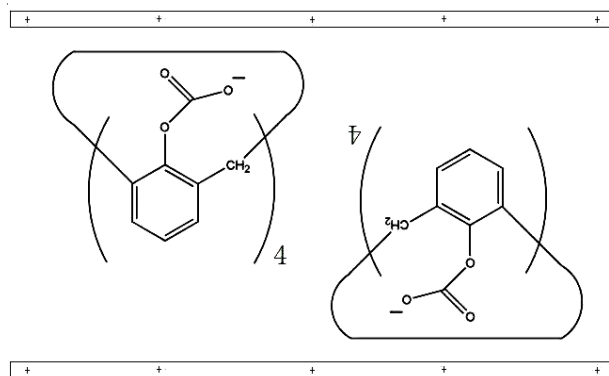


Fig. 2. Schematic representation of the possible arrangement of CMCS-LDHs

Infrared spectroscopy: The FT-IR spectra of CMCS and the CMCS-LDHs powder are shown in Fig. 3. In the infrared spectrum of the as-synthesized sodium salt of CMCS, a broad strong absorption band at 3444 cm^{-1} is observed, which can be attributed to OH combination stretching vibrations of hydroxyl groups and physically adsorbed water. An absorption at 2929 cm^{-1} is due to the stretching vibration of $-CH_2-$. Two strong bands at 1599 and 1554 cm^{-1} are attributed to the stretching vibrations of $C=C$ in the benzene ring. The band at 1415 cm^{-1} is attributed to the symmetric stretching vibrations of carboxylate $-COO^-$. Bands at 1160 , 1036 cm^{-1} are assigned to absorption of $C-O$, $C-O-C$ of CMCS. In the case of the CMCS-LDHs powder, most bands of CMCS show no obvious change upon intercalation into layered double hydroxides (Fig. 3b). The symmetric stretching band of $-COO^-$ moves slightly toward to low frequency, at 1400 cm^{-1} . This spectral change may be related to the formation of hydrogen bonding between the carboxylate and the hydroxyl in layered double hydroxides layer. Moreover, the metal-hydroxyl (M-OH) stretching modes of layered double hydroxides layer appear at 425 cm^{-1} .

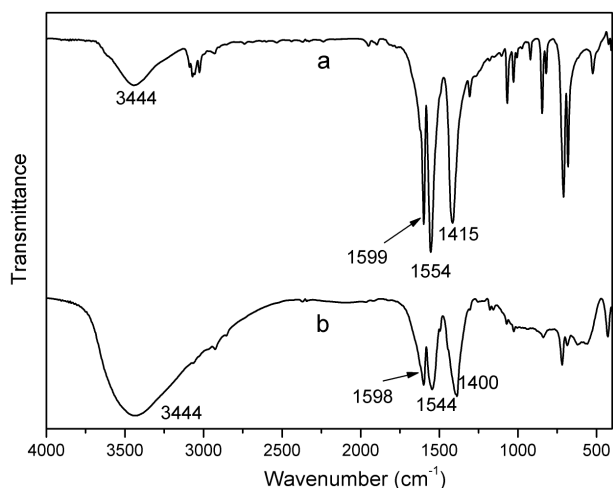


Fig. 3. FT-IR spectra of (a) the CMCS, (b) the CMCS-LDHs powder

SEM and EDX: The morphology of the PAO/Al substrate and CMCS-LDHs film was studied by scanning electron microscopy (SEM). The top surface (Fig. 4A) is the CMCS-LDHs film after crystallization on the PAO/Al substrate at 70 °C for 48 h. The curved hexagonal faces of the layered double hydroxides microcrystal can be clearly observed perpendicular to the substrate over the entire substrate surface. The edge-view of the CMCS-LDHs film (Fig. 4B) demonstrates that only a monolayer of the layered double hydroxides crystals with a thickness of *ca.* 0.5 μm was assembled on the PAO/Al substrate. These images indicate that the *ab*-face of layered double hydroxides microcrystals is predominantly perpendicular with respect to the substrate. This observation can be confirmed by energy dispersive X-ray (EDX) analysis, displayed in Fig. 4C. The Zn/Al distribution ranges from 1.3 to 2.0 along EDX line scanning over the layered double hydroxides film and a part of the PAO/Al substrate. At depths below 500 nm, however, the Zn profile of the EDX rapidly decreases to almost zero, indicating the absence of the Zn species inside the substrate.

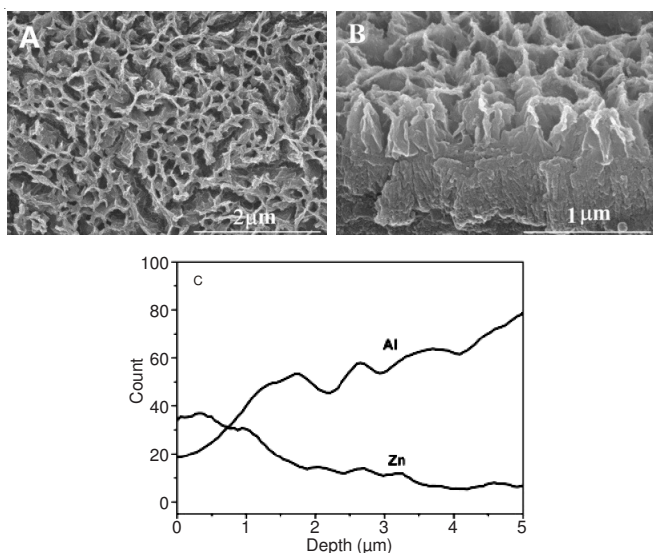


Fig. 4. SEM images of (A) surface-view of the CMCS-LDHs film on PAO/Al substrate, (B) edge-view of the CMCS-LDHs film, (C) the energy dispersive X-ray line scan of the edge-view of the film

Conclusion

The investigation has led to a new finding for the intercalation of a water-soluble macrocyclic molecule, CMCS, in the interlayer of layered double hydroxides. In both powder and film samples, CMCS molecules adopt a monolayer arrangement, with the axis of the cavity perpendicular to the layered double hydroxides sheets. The XRD results show that the basal spacing of the resulting CMCS-LDHs material is larger than that of NO_3 -LDHs. These results confirm the intercalation of CMCS in the interlayer galleries of LDHs. The SEM images indicate that the *ab*-face of layered double hydroxides microcrystals is predominantly perpendicular with respect to the substrate. Compared with CMCS-LDHs powder sample, the structured CMCS-LDHs film exhibits the advantages of more convenient operation. It can be expected that this CMCS functionalized inorganic layered film may have potential application in the field of industrial adsorption, separation and inclusion.

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REFERENCES

- X.L. Liu, Q. Wang, N.Q. Zhao, M. Wei and X. Duan, *Asian J. Chem.*, **23**, 5311 (2011).
- Y.F. Zhao, S. He, M. Wei, D.G. Evans and X. Duan, *Chem. Commun.*, **46**, 3031 (2010).
- G.R. Williams, T.G. Dunbar, A.J. Beer, A.M. Fogg and D. O'Hare, *J. Mater. Chem.*, **16**, 1231 (2006).
- L. Jin, X.Y. Ni, X.L. Liu and M. Wei, *Chem. Eng. Technol.*, **33**, 82 (2010).
- S.P. Newman and W. Jones, *New J. Chem.*, **22**, 105 (1998).
- B.F. Sels, D.E. De Vos and P.A. Jacobs, *Angew. Chem., Int. Ed.*, **44**, 310 (2005).
- X.Q. Hou and R.J. Kirkpatrick, *Chem. Mater.*, **14**, 1195 (2002).
- Z.P. Xu and P.S. Braterman, *J. Phys. Chem. C*, **111**, 4021 (2007).
- G. Hu and D. O'Hare, *J. Am. Chem. Soc.*, **127**, 17808 (2005).
- E. Gardner, K.M. Huntoon and T.J. Pinnavaia, *Adv. Mater.*, **13**, 1263 (2001).
- L. Li, R.Z. Ma, Y. Ebina, N. Iyi and T. Sasaki, *Chem. Mater.*, **17**, 4386 (2005).
- D.P. Yan, J. Lu, J. Ma, S.H. Qin, M. Wei, D.G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, **50**, 7037 (2011).
- S. Li, J. Lu, H. Ma, J. Xu, D.P. Yan, M. Wei, D.G. Evans and X. Duan, *Langmuir*, **27**, 11501 (2011).
- J. Zhao, X. Kong, W.Y. Shi, M. Shao, J.B. Han, M. Wei, D.G. Evans and X. Duan, *J. Mater. Chem.*, **21**, 13926 (2011).
- A.V. Maffei, P.M. Budd and N.B. Mckeown, *Langmuir*, **22**, 4255 (2006).
- W.Y. Shi, Y. Lin, X. Kong, S. Zhang, Y. Jia, M. Wei, D.G. Evans and X. Duan, *J. Mater. Chem.*, **21**, 6088 (2011).
- J.B. Han, X. Xu, X. Rao, M. Wei, D.G. Evans and X. Duan, *J. Mater. Chem.*, **21**, 2126 (2011).
- J.B. Han, Y. Dou, M. Wei, D.G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, **49**, 2171 (2010).
- L. Li, R.Z. Ma, Y. Ebina, K. Fukuda, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, **129**, 8000 (2007).
- S. Huang, X. Cen, H. Peng, S. Guo, W. Wang and T. Liu, *J. Phys. Chem. B*, **113**, 15225 (2009).
- X.L. Liu, M. Wei, D.G. Evans and X. Duan, *Chem. Eng. Sci.*, **64**, 2226 (2009).
- X.L. Liu, Q. Wang, D.G. Geng, M. Wei and X. Duan, *Asian J. Chem.*, **24**, 101 (2012).
- P.E. Georghiou, A.H. Tran, S.S. Stroud and D.W. Thompson, *Tetrahedron*, **62**, 2036 (2006).
- J.S. Wang and C.D. Gutsche, *J. Am. Chem. Soc.*, **120**, 12226 (1998).
- M.R. Yafitian, M. Burgard, C.B. Dieleman and D. Matt, *J. Membr. Sci.*, **144**, 57 (1998).
- S. Kunsagi-Mate, K. Szabo, I. Bitter, G. Nagy and L. Kollar, *Tetrahedron Lett.*, **45**, 1387 (2004).
- P.E. Georghiou, A.H. Tran, S.S. Stroud and D.W. Thompson, *Tetrahedron*, **62**, 2036 (2006).
- K. Iwamoto and S. Shinkai, *J. Org. Chem.*, **57**, 7066 (1992).
- N. Douteau-Guevel, A.W. Coleman, J.P. Morel and N. Morel-Desrosier, *J. Chem. Soc., Perkin Trans. II*, 629 (1999).
- C. Bonal, Y. Israeli, J.P. Morel and N. Morel-Desrosiers, *J. Chem. Soc., Perkin Trans. II*, 1075 (2001).
- F. Prat, C. Mart, S. Nonell, X.J. Zhang, C.S. Foote, R.G. Moreno, J.L. Bourdelande and J. Font, *Phys. Chem. Chem. Phys.*, **3**, 1638 (2001).
- M. Makha, C.L. Raston, A.N. Sobolev and P. Turner, *Crystal Growth Design*, **6**, 224 (2006).
- S. Kim, J.S. Kim, S.K. Kim, I.H. Suh, S.O. Kang and J. Ko, *Inorg. Chem.*, **44**, 1846 (2005).
- B.F. Sels, D.E. DeVos and P.A. Jacobs, *J. Am. Chem. Soc.*, **129**, 6916 (2007).
- L.P. Cardoso, R. Celis, J. Cornejo and J.B. Valim, *J. Agric. Food Chem.*, **54**, 5968 (2006).
- X.L. Liu, M. Wei, Z.L. Wang, D.G. Evans and X. Duan, *J. Phys. Chem. C*, **112**, 17517 (2008).
- X.L. Liu, M. Wei, F. Li and X. Duan, *AIChE J.*, **53**, 1591 (2007).
- H.Y. Chen, F.Z. Zhang, S.S. Fu and X. Duan, *Adv. Mater.*, **18**, 3089 (2006).
- S. Sasaki, S. Aisawa, H. Hirahara, A. Sasaki, H. Nakayama and E. Narita, *J. Solid State Chem.*, **179**, 1129 (2006).