

No part of this digital document may be reproduced, stored in a retrieval system or transmitted commercially in any form or by any means. The publisher has taken reasonable care in the preparation of this digital document, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained herein. This digital document is sold with the clear understanding that the publisher is not engaged in rendering legal, medical or any other professional services.

Chapter 7

**MATRIX VISCOSITY-DEPENDENCE OF
CD SPECTRA OF A CHIRAL SCHIFF BASE
MANGANESE(III) COMPLEX**

Takashiro Akitsu, Yu Okamoto
and Keisuke Nidaira*

Department of Chemistry, Faculty of Science,
Tokyo University of Science, Shinjuku-ku, Tokyo, Japan

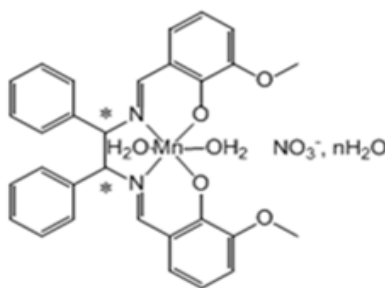
ABSTRACT

Catalytic and magnetic Schiff base Mn(III) complexes afford various crystal structures, such as hydrogen-bonded chains or dimers, directly bonded dimers, and isolated monomers, associated with axial ligands. Among them, isolated monomers may be suitable for discussion of spectroscopic properties in both solid states and soft mater matrix. A new chiral Schiff base Mn(III) complex having a (*1R,2R*)-(+)- diphenyl-1,2-diamine moiety was prepared and characterized structurally to be a six-coordinated coordination geometry. Magnetic measurement of bulk complex and its cast film of PMMA revealed preservation of the structure. CD spectra were measured in the solid state, as a PMMA cast film, various concentrations of acetone solutions of PMMA, and as solutions of several organic solvents. As solutions, solvatochromism was observed slightly depending on polarity of solvents. As PMMA cast film and solutions, intensity changes (positive increasing) of a CD peak around 420 nm assigned as an artifact CD peak of solid state indicated depending on viscosity of matrix. Limitation of molecular motion increasing molecular orientation in a matrix results in this correlation to the intensity of an artifact CD peak.

* E-mail address: akitsu@rs.kagu.tus.ac.jp.

INTRODUCTION

In recent years, organic/inorganic hybrid materials containing transition metal complexes have been developed widely in view of controlling supramolecular assemblies for magnetic properties [1-3] and molecular orientation [4-8]. For photo-induced molecular orientation, polarized electronic and IR spectra may be valid for separated observation of individual components in hybrid materials such as PMMA polymer cast film. When hybrid materials contain a sole chiral component, CD spectra may be useful for separated observation of the chiral one, which can be also interpreted with the aid of TD-DFT calculations closely. However, it is sometimes serious problem that CD spectra in the solid state may appear artifact peaks [9]. Environment of a polymer matrix is flexible being possible for occurring molecular isomerization or keeping anisotropic molecular orientation [10]. In this way, investigation of matrix viscosity-dependence [11] of the intensity of artifact CD peaks due to anisotropy of chiral molecules may provide new spectral information of organic/inorganic hybrid materials [12]. Herein, we prepared a new chiral Schiff base Mn(III) complex (Scheme 1) and measured its CD spectra measured as solid state, PMMA cast film, PMMA solution of various concentration, and solutions of various organic solvents.



Scheme 1.

EXPERIMENTAL SECTION

Materials

All reagents and solvents (Wako, TCI, and Aldrich) were commercially available and were used as purchased without further purification.

Preparations

Preparation of Mn(III) complex. To a solution of *o*-vaniline (0.3064 g, 2.00 mmol) dissolved in methanol (40 mL), (*1R,2R*)-(+)-diphenyl-1,2-diamine (0.2147 g, 1.00 mmol) was added dropwise and stirred at 313 K for 2 h to give yellow solution of ligand. Methanol solution (20 mL) of manganese(II) acetate tetrahydrate (0.2492 g, 1.00 mmol) and neodymium(III) nitrate (0.4851 g, 1.00 mmol) was added to the resulting solution to give brown solution of the complex. After stirring at 373 K for 4 h, the resulting black solution

was filtrated to obtain black prismatic precipitates. Yield 0.2821 g (41.8 %). Anal. Calc. for $C_{60}H_{70}Mn_2N_6O_{24}$ (two molecules as crystals) C, 57.06; H, 4.79; N, 6.65. Found: C, 57.46; H, 4.54; N, 6.69 %. IR (KBr (cm^{-1})): 579, 648, 734, 858, 994, 1078, 1219, 1250, 1300, 1338, 1438, 1467, 1548, 1600, 1620 (C=N), 2831, 2932, 2998, 3008, 3056, 3419.

Physical Measurements

Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 4200 plus spectrophotometer equipped with polarizer in the range of 4000-400 cm^{-1} at 298 K. Diffuse reflectance or absorption electronic spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer equipped with an integrating sphere in the range of 800-200 nm at 298 K. Circular dichroism (CD) spectra were measured as KBr pellets on a JASCO J-820 spectropolarimeter in the range of 800-200 nm at 298 K. The magnetic properties were investigated with a Quantum Design MPMS-XL superconducting quantum interference device magnetometer (SQUID) an applied field 5000 Oe in a temperature range 5-300 K. Powder samples were measured in a pharmaceutical cellulose capsule.

X-ray Crystallography

Crystallographic data. T = 173 K. $C_{60}H_{70}Mn_2N_6O_{24}$, crystal size 0.13 mm \times 0.12 mm \times 0.12 mm, $M_w = 1369.10$, monoclinic, space group $P2_1(\#4)$, a = 12.0373(9) Å, b = 10.6190(8) Å, c = 24.7967(18) Å, $\beta = 99.1700(10)^\circ$, V = 3129.1(4) Å³, Z = 2, $D_{calc} = 1.453$ mg/m³, F(000) = 1428, $R_1 = 0.0535$, $wR_2 = 0.1446$ (9906 reflections), S = 0.998, Flack parameter = 0.041(18). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

RESULTS AND DISCUSSION

Crystal Structures

Figure 1 depicts crystal structure of the Mn(III) complex having a diphenyl-1,2-diamine moiety, which affords a six-coordinated octahedral coordination geometry. An asymmetric unit contains two independent molecules crystallographically. No remarkable geometric parameters could be found in the structure [13-19]. Hydrogen atoms of crystalline water could not be included in the model, because they could not be located based on electronic density nor estimation by hydrogen bonds.

Magnetic Properties

Figure 2 exhibits temperature and field dependence of magnetization of the Mn(III) complex as bulk and in a PMMA cast film. As the crystal structure of mononuclear complex

without specific magnetic interactions, both data indicate paramagnetism except for diamagnetic contribution of PMMA, which suggest that molecular structure is also kept in the cast film [3, 7, 8].

CD Spectra

The CD spectra and the corresponding electronic absorption spectra were measured as various solutions of different organic solvents (Figure 3). As solutions, solvatochromism was observed slightly depending on not viscosity but polarity of solvents, which suggest that molecular structure is also kept in the solutions. For example, one of the remarkable peaks appeared at 330 nm in methanol (0.58 mPas at 293 K), 331 nm in acetone (0.32 mPas at 293 K), and 338 nm in chloroform (0.56 mPas at 293 K). Figure 3 also shows comparison of absorption and CD spectra of the complex in the solid state (KBr), PMMA cast film and acetone solution. It should be noted that an characteristic artifact CD peak for the solid states was appeared around 420 nm, which also appeared in PMMA matrix, while disappeared in solutions. In PMMA matrix, the artifact CD peak characteristic to solid state [9, 20] could be observed weakly.

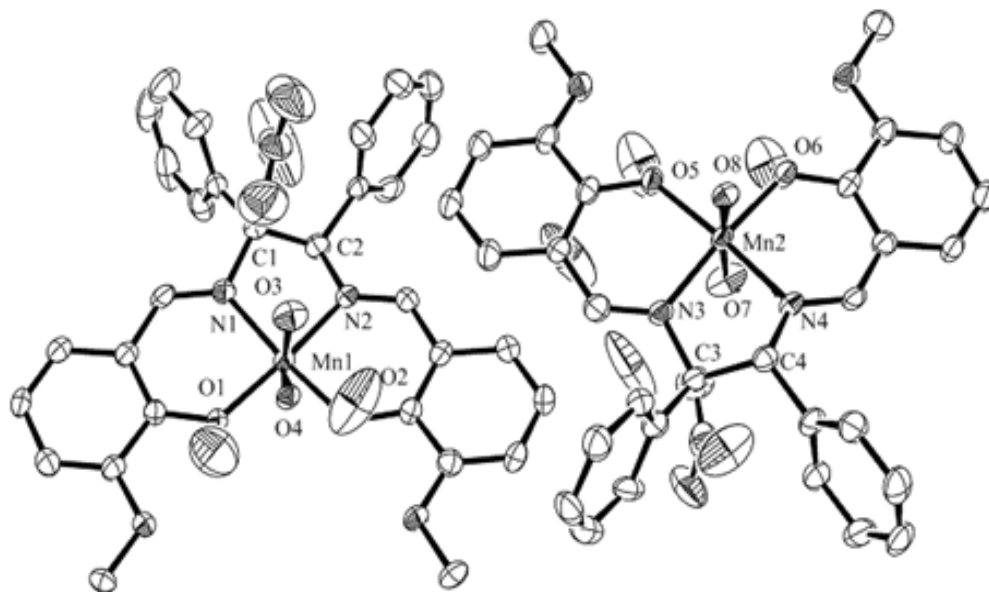


Figure 1. Molecular structures showing selected atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and angles (°): Mn1-O1 = 1.878(3), Mn1-O2 = 1.887(3), Mn1-N1 = 1.984(3), Mn1-N2 = 1.993(4), Mn1-O3 = 2.217(6), Mn1-O4 = 2.280(5), Mn2-O3 = 1.887(3), Mn2-O4 = 1.894(3), Mn2-N2 = 1.980(3), Mn2-N1 = 1.990(4), Mn2-O5 = 2.284(6), Mn2-O6 = 2.286(5), O1-Mn1-O2 = 92.36(12), O1-Mn1-N1 = 92.53(14), O2-Mn1-N1 = 174.66(15), O1-Mn1-N2 = 175.11(14), O2-Mn1-N2 = 92.53(13), N1-Mn1-N2 = 82.58(14), C1-N1-Mn1 = 112.7(3), C2-N2-Mn1 = 113.6(3), O3-Mn2-O4 = 92.68(12), O4-Mn2-N4 = 92.07(14), O3-Mn2-N4 = 175.00(14), O3-Mn2-N3 = 92.56(13), O4-Mn2-N3 = 172.88(14), N2-Mn2-N3 = 82.84(14), C4-N4-Mn2 = 112.9(3), C3-N3-Mn2 = 112.2(3).

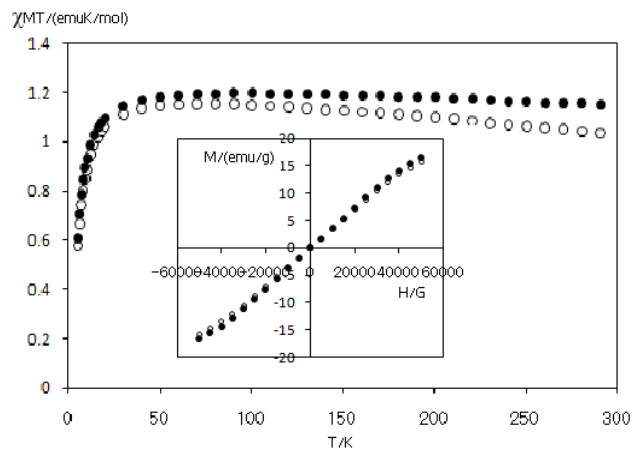


Figure 2. Temperature dependence of $\chi_M T$ values of bulk complex (filled circles) and in a PMMA film (empty marks) at 0.5 T. [inset] Field dependence of magnetization of bulk complex (filled marks) and in a PMMA film (empty marks) at 5 K.

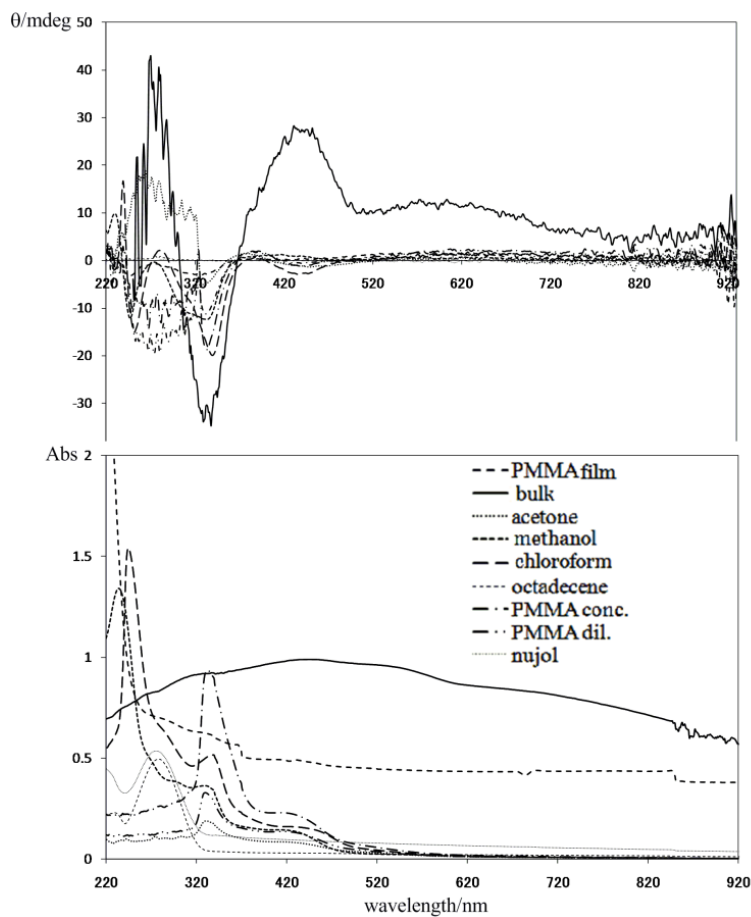


Figure 3. Absorption and CD spectra of the complex in the solid state (KBr pellet), PMMA cast film and acetone solution.

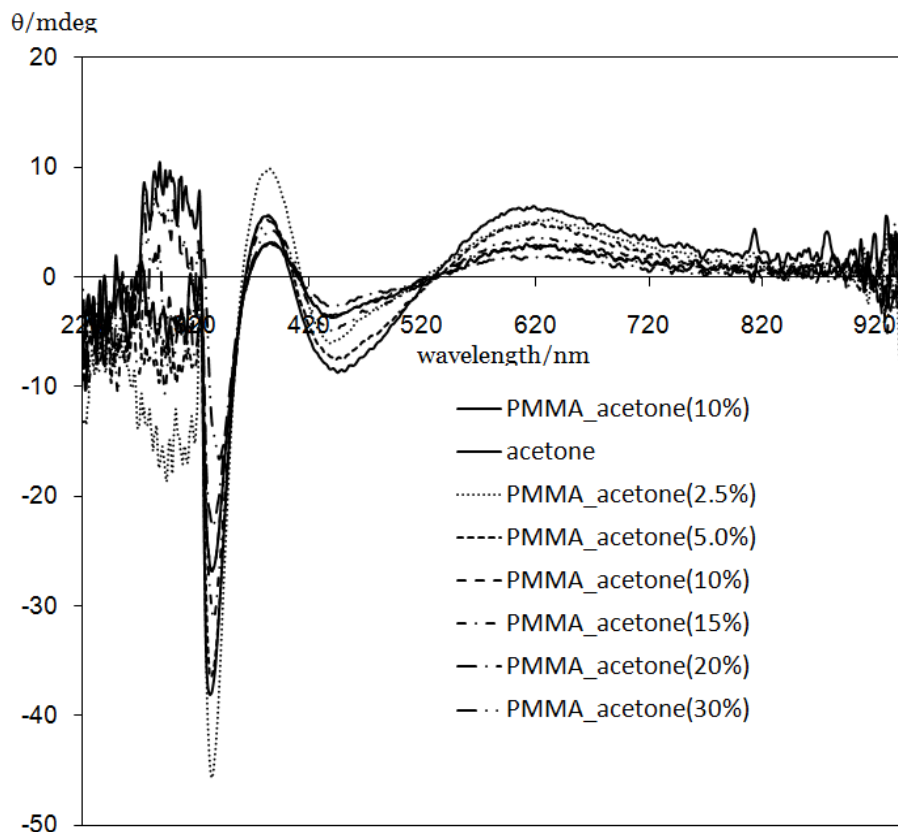


Figure 4. Concentration (viscosity) dependence of the CD spectra of PMMA acetone solutions of the complexes. The plain line denotes a film made from a “PMMA acetone (10%)” solution.

Figure 4 indicates concentration or viscosity-dependence of the CD spectra of PMMA acetone solutions of the complexes. As PMMA cast film and solutions, intensity changes (positive increasing) of a CD peak around 420 nm assigned as an artifact CD peak of solid state indicated depending on viscosity of matrix. Spectral features in PMMA acetone solutions are similar to that of various organic solvents. In this way, restricted molecular motion, namely molecular orientation in a matrix, resulted in this correlation with respect to the intensity of an artifact CD peak [11].

CONCLUSION

As for solid state CD spectroscopy, attempts to decrease artifact peaks caused by anisotropic molecular orientation have been investigated by means of theoretical approach of CD and LD as well as instrumental improvement [21-35]. Indeed, as for solutions, CD spectra without contribution of some terms providing artifact peaks of solid state is cancelled may normally be observed because of isotropic molecular orientation due to free motion (rotation) of chiral molecules. In this system of PMMA polymer matrix suggesting anisotropic molecular orientation as well as restricted molecular motion, we have found matrix viscosity-

dependence of the intensity of artifact peaks of CD spectra for the first time to our knowledge. The intensity of the peaks may be classified into moderate degree between solid state and (diluted) solutions.

ACKNOWLEDGMENT

The author thanks the Materials Design and Characterization Laboratory, Institute for Solid State Physics University of Tokyo for the SQUID facilities.

SUPPLEMENTARY DATA

Crystallographic Data

CCDC 810827 contains the supplementary crystallographic data. These data can be obtained free of charge *via*

<http://www.ccdc.cam.ac.uk/conts/retrieving>.

html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

- [1] Akitsu, T.; Nishijo, J. *J. Magn. Magn. Mater.* 2008, 320, 1586-1590.
- [2] Akitsu, T.; Nishijo, J. *J. Magn. Magn. Mater.* 2007, 315, 95-100.
- [3] Akitsu, T. *J. Magn. Magn. Mater.* 2009, 321, 207-212.
- [4] Aritake, Y.; Takanashi, T.; Yamazaki, A.; Akitsu, T. *Polyhedron*. 2011, 30, 886-894.
- [5] Akitsu, T.; Tanaka, R. *Curr. Phys. Chem.* 2011, 1, 82-89.
- [6] Akitsu, T.; Itoh, T. *Polyhedron*. 2010, 29, 477-487.
- [7] Akitsu, T.; Ishioka, C. *Asian Chem. Lett.* 2010, 14, 37-51.
- [8] Akitsu, T.; Ishioka, C.; Itoh, T. *Cent. Eur. J. Chem.* 2009, 7, 690-696.
- [9] Kuroda, R.; Harada, T.; Shindo, Y. *Rev. Sci. Instr.* 2001, 72, 3802-3810.
- [10][10] Schellman, J.; Jensen, H. P. *Chem. Rev.* 1987, 87, 1359-1399.
- [11] Gil, M.; Dobkowski, J.; Wiosna-Salyga, G.; Urbanska, N.; Fita, P.; Radzewicz, C.; Pietraszkiewicz, M.; Borowicz, P.; Marks, D.; Glasbeek, M.; Waluk, J. *J. Am. Chem. Soc.* 2010, 132, 13472-13485.
- [12] Hicks, M. R.; Kowalski, J.; Rodger, A. *Chem. Soc. Rev.* 2010, 39, 3380-3393.
- [13] Akitsu, T.; Takeuchi, Y.; Einaga, Y. *Acta Cryst.* 2005, E61, m772-m774.
- [14] Ashmawy, F. M.; McAuliffe, C. A.; Parish, R. V.; Tames, J. *J. Chem. Soc. Dalton Trans.* 1985, 1391-1397.
- [15] Aurangzeb, N.; Hulme, C. E.; McAuliffe, C. A.; Pritchard, R. G.; Watkinson, M.; Bermejo, M. R.; Garcia-Deibe, A.; Rey, M.; Sanmartin, J.; Sousa, A. *J. Chem. Soc. Chem. Commun.* 1994, 1153-1155.

-
- [16] Bermejo, M. R.; Castineiras, A.; Garcia-Montegudo, J. C.; Rey, M.; Sousa, A.; Watkinson, M.; McAuliffe, C. A.; Pritchard, R. G.; Beddoes, R. L. *J. Chem. Soc. Dalton Trans.* 1996, 2935-2944.
- [17] Korendovych, I. V.; Rybak-Akimova, E. V. *Acta Cryst.* 2004, C60, m82-m84.
- [18] Martinez, D.; Motecalli, M.; Watkinson, M. *Acta Cryst.* 2002, C58, m258-m260.
- [19] Reger, T. S.; Janda, K. D. *J. Am. Chem. Soc.* 2000, 122, 6929-6934.
- [20] Bing, Y.; Selassie, D.; Paradise, R. H.; Isborn, C.; Kramer, N.; Sadilek, M.; Kaminsky, W.; Kahr, B. *J. Am. Chem. Soc.* 2010, 132, 7454-7465.
- [21] Schellaman, J.; Jensen, H. P. *Chem. Rev.* 1987, 87, 1359-1399.
- [22] Tinoco, I.; Mickols, W.; Maestre, M. F.; Bustamante, C. *Annu. Rev. Biophys. Biophys. Chem.* 1987, 16, 319-349
- [23] Clabom, K.; Isbom, C.; Kaminsky, W.; *Angew. Chem. Int. Ed. Engl.* 2008, 47, 5706-5717.
- [24] Kaminsky, W. *Rep. Prog. Phys.* 2000, 63, 1575-1640.
- [25] Shindo, Y.; Nakagawa, M. *Appl. Spectrosc.* 1985, 39, 32-38.
- [26] Shindo, Y.; Nakagawa, M.; Ohmi, T. *Appl. Spectrosc.* 1985, 39, 860-868.
- [27] Hips, K. W.; Crosby, G. A. *J. Phys. Chem.* 1979, 83, 555-562.
- [28] Goldstein, D.H. *Polarized Light*. New York, NY, USA, Marcel Dekker; 2003.
- [29] Kobayashi, J.; Uesu, Y.; Takehara, H. *J. Appl. Crystallogr.* 1983, 16, 212-219.
- [30] Kaminsky, W.; Clabom, K.; Kahr, B. *Chem. Soc. Rev.* 2004, 33, 514-525.
- [31] Kahr, B.; Bing, Y.; Kaminsky, W.; *Chem. Int. Ed.* 2009, 48, 3744-3748.
- [32] Bing, Y.; Selassie, D.; Paradise, R. H.; Isbom, C.; Kramer, N.; Sadilek, M.; Kaminsky, W.; Kahr, B. *J. Am. Chem. Soc.* 2010, 132, 7454-7465.
- [33] Kaminsky, W.; Geday, M. A.; Herreros-Cedr s, J.; Kahr, B. *J. Phys. Chem. A* 2003, 107, 2800-2807.
- [34] Kaminsky, W.; Herreros-Cedr s, J.; Geday, M. A.; Kahr, B. *Chirality* 2004, 16, S55-S61.
- [35] Clabom, K.; Chu, A. S.; Jang, S. H.; Su, F. Y.; Kaminsky, W.; Kahr, B. *Cryst. Growth Des.* 2005, 5, 2117-2123.