



(R)-1,1'-联萘手性单元通过溶胶凝胶法合成杂化硅干凝胶

成义祥* 宋金峰 陈令武 邹小伟

(南京大学化学化工学院, 南京 210093)

关键词: (R)-2,2'-联萘酚; 有机硅; 溶胶凝胶; Heck 反应

中图分类号: O613.22; O625.31+3

文献标识码: A

文章编号: 1001-4861(2005)04-0561-04

Silica Hybrid Xerogel Incorporating (R)-2,2'-bis(methoxyethoxymethoxy)-1,1'-binaphthyl Unit via Sol-Gel Process

CHENG Yi-Xiang* SONG Jin-Feng CHEN Ling-Wu ZOU Xiao-Wei

(School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093)

Abstract: Precursor molecule (R)-6,6'-bis(triethoxysilyl)ethen-2-yl)-2,2'-di(methoxyethoxymethoxy)-1,1'-binaphthyl (R-2) was synthesized by Pd-catalyzed Heck reaction of (R)-6,6'-dibromo-2,2'-di(methoxyethoxymethoxy)-1,1'-binaphthyl (R-1) intermediate with vinyltriethoxysilane. The hydrolysis and polycondensation of the precursor R-2 produced the corresponding xerogel. Both precursor and xerogel were analysed by NMR, FTIR, UV, CD spectra, fluorescent spectroscopy, polarimetry and elemental analysis. The precursor and xerogel can emit strong blue fluorescence and are expected to have a potential application in the separation of chiral molecules as fluorescent sensor. The precursor exhibits strong Cotton effect in its circular dichroism (CD) spectrum indicating a highly rigid structure.

Key words: (R)-2,2'-BINOLs; organic silicon; sol-gel; Heck reaction

0 Introduction

Sol-gel-derived hybrid organic-inorganic materials are receiving much attention since they can exhibit properties associated with both the organic moieties (optical, electrical, molecular imprinting) and inorganic amorphous framework (porosity, hydrophilicity)^[1~4]. The mild reaction conditions of the sol-gel approach can control the formation of a deliberate tailoring of hybrid organic-inorganic materials by hydrolysis and polycondensation of the precursors functionalized by hydrolysable triethoxysilane groups^[5]. The preparation of a molecularly defined hybrid network containing al-

ternating chiral centers and siloxane units was achieved by sol-gel hydrolysis of suitable precursors containing one non-hydrolyzable silicon-carbon bond. The hybrid materials are expected to have a potential application in the electro-optical sensors, asymmetric catalysis, enantioselective and molecular recognition by controlling the chiral organic substructure and inorganic framework^[1,6,7]. Optically reactive binaphthyl molecules can exhibit remarkably stable chiral configuration as well as high chiral induction. Xerogel with chiral binaphthyl moieties have been devoted to preparing the novel structure precursors for the separation of chiral amines or α -aminoacides in chiral

收稿日期: 2004-09-06。收修改稿日期: 2004-12-10。

江苏省自然科学基金(No.BK2004086)和国家自然科学基金(No.20474028)资助项目。

*通讯联系人。E-mail: yxcheng@nju.edu.cn

第一作者: 成义祥, 男, 38岁, 副教授; 研究方向: 金属有机和有机高分子化学。

HPLC, useful chiral ligands in asymmetric catalysis and highly selective chiral luminescent sensors^[8-10].

The aim of this work is the elaboration of functional materials based on chiral building blocks for asymmetric catalysis and luminescent sensor. The precursor R-2 molecule derived from BINOL-derivative was synthesized by Pd-catalyzed Heck reaction of intermediate R-1 with vinyltriethoxysilane. The hydrolysis and polycondensation of the precursor gives rise to the corresponding organic-inorganic hybrid xerogel by sol-gel transformation of precursor R-2.

1 Experimental

1.1 Instruments and reagents

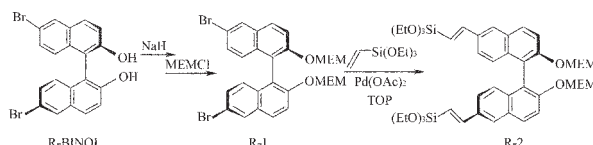
All reactions were performed under nitrogen or argon atmosphere using Schlenk tube techniques. ¹H, ¹³C and ²⁹Si NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers. Deuterated chloroform was used as NMR solvent and chemical shifts were reported as δ -values in parts per million relative to tetramethylsilane, *J*-values were in Hz. Xerogel ²⁹Si-NMR was recorded on a Bruker WP 250 FT AM 300 apparatus. Fluorescent spectra were determined on a Model 8100 spectrometer. Optical rotations were measured on a Perkin-Elmer polarimeter 241. Circular dichroism (CD) spectra were carried on a JASCO J-810 spectropolarimeter. Methoxyethoxymethyl (MEM) chloride was purchased from Aldrich and used without further purification. In experiments requiring dry solvents, THF and diethyl ether were distilled from sodium-benzophenone, DMF was distilled from CaH₂, and CH₂Cl₂ was distilled from P₂O₅.

1.2 Synthesis of Precursor R-2 and Xerogel

(*R*)- and (*S*)-1,1'-bi-2-naphthol (BINOL) were synthesized and resolved according to the literature (90%, >99.9% ee)^[11,12]. The intermediate R-1 was synthesized as described in the literature^[2,13].

Precursor R-2 molecule was synthesized by Pd-catalyzed Heck reaction of intermediate R-1 with vinyltriethoxysilane (Scheme 1)^[14,15]. R-1 (1.24 g, 2 mmol), 0.4% Pd(OAc)₂ (2.3 mg), 2.4% P(*o*-C₆H₄CH₃)₃ (TOP) (14.8 mg) and 5 equivalents of Et₃N (1.7 mL) were dissolved in 25 mL of freshly distilled DMF, followed by the addition of vinyltriethoxysilane (0.9 mL, 4.0 mmol) via a syringe. After stirring and heating at 105 °C overnight under Ar and at 115 °C for 2 h, the mix-

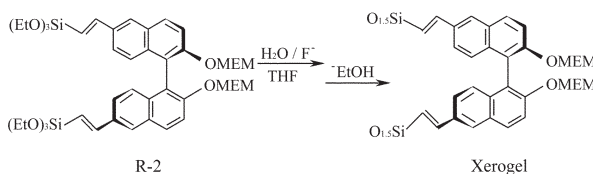
ture was cooled down to room temperature. After filtration of the resulting triethylammonium salt and catalyst, the solvent was removed at reduced pressure with an oil heating bath at 100 °C. 20 mL of ether was added to the viscous residue under Ar to precipitate out a large amount white triethylammonium salt. After filtration, the solution was evaporated at reduced pressure under Ar. The yellow viscous product R-2 was dried in vacuo overnight under 80 °C oil bath. The final yield was 93% (1.5 g). The precursor R-2 showed a moderate to good solubility in ethanol, ether, THF, CH₂Cl₂ and CHCl₃.



Scheme 1 Synthesis process of precursor R-2

R-2 ¹H NMR (CDCl₃): δ 1.25 (t, 18H, *J*=14 Hz), 3.25 (s, 6H), 3.27~3.44 (m, 8H), 3.87 (q, 12H, *J*=14 Hz), 5.10 (dd, 4H, *J*=26, 6 Hz), 6.16 (d, 2H, *J*=20 Hz), 7.07 (d, 2H, *J*=8 Hz), 7.27 (d, 2H, *J*=6 Hz), 7.41 (d, 2H, *J*=8 Hz), 7.59 (d, 2H, *J*=8 Hz), 7.85 (s, 2H), 7.93 (d, 2H, *J*=10 Hz); ¹³C NMR (CDCl₃): δ 18.29, 58.61, 58.88, 67.49, 71.37, 94.15, 117.24, 117.64, 121.04, 123.73, 125.79, 127.71, 129.77, 129.93, 133.48, 134.15, 149.01, 153.24; ²⁹Si NMR: δ -55.97; [α]_D²⁵ = -123.8 (c 0.5, THF); Anal. Calcd For C₄₄H₆₂O₁₂Si₂ (%) C 63.11, H 7.08; found C 62.98, H 7.44.

The hydrolysis and polycondensation of the precursor R-2 is shown in Scheme 2. The preparation of xerogel was performed in THF using saturated NH₄F as fluoride catalyst^[1,2,7,15]. R-2 (840 mg, 1 mmol) was dissolved in 3 mL of THF, and then 54 μ L of H₂O and 13 μ L of saturated NH₄F solution were dropped into the above solution, respectively. The solution was vigorously stirred at room temperature until sol being formed. The sol was allowed to stand for one week and give rise to yellow solid xerogel. The xerogel was



Scheme 2 Sol-Gel process of xerogel

scattered to get a powder, which was washed with THF and ether for several times. The xerogel was dried overnight in vacuo. The final product was obtained in 80% yield (490 mg). Anal. calcd for $C_{32}H_{32}O_9Si_2$: C 60.20, H 5.46; found C 62.32, H 5.23.

2 Results and discussion

UV spectra of precursor R-2 and the intermediate R-1 were determined in THF solution (Fig.1). The strongest absorption of precursor R-2 was observed at 271 nm ($\varepsilon_{271}=8.58\times10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), and the largest absorption λ_{max} appeared at 300 nm ($\varepsilon_{300}=3.81\times10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). By comparing the UV absorption wavelengths of the precursor R-2 with R-1, the stronger peak observed is 216 nm and 236 nm ($\varepsilon_{216}=9.56\times10^4$ and $\varepsilon_{236}=9.17\times10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), respectively, the largest absorption λ_{max} appears at 285 nm ($\varepsilon_{285}=2.00\times10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). It was concluded that there was a larger red-shift in the electronic absorption of the precursor due to the effective π conjugated segment of naphthyl group with vinyltriethoxysilane. The precursor R-2 and xerogel can emit very strong blue light under Ultraviolet light (366 nm), but R-1 can not show visible fluorescence. The precursor R-2 and xerogel showed strong blue fluorescence due to the extended π -electronic system. The fluorescent wavelengths $\lambda_{\text{max}}^{\text{F}}$ of precursor R-2 in THF solution are 406 nm, but in the KBr solid state, the emitting wavelength of xerogel appears at 431 nm (Fig.2). It can be attributed to the interaction between the chromophores and formation of fluorescent dye aggregates within the hybrid amorphous xerogel^[2].

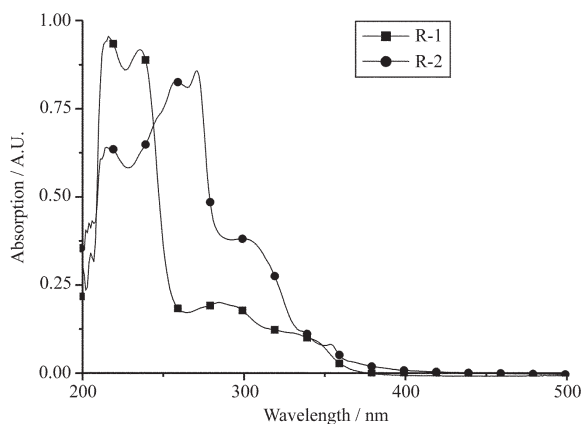


Fig.1 UV spectra of R-1 and R-2

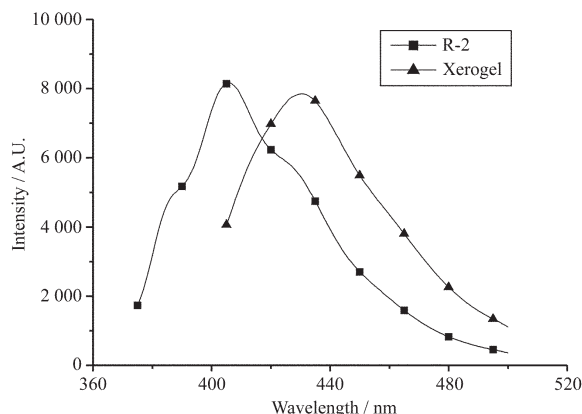


Fig.2 Fluorescent spectra of R-2 ($\lambda_{\text{ex}}=328\text{ nm}$) and Xerogel ($\lambda_{\text{ex}}=377\text{ nm}$)

The optical rotation ($[\alpha]_{\text{D}}^{25}$) of the precursor R-2 was -123.8 (c 0.5, THF), but $[\alpha]_{\text{D}}^{25}$ of R-1 was $+18.5$ (c 0.4 THF)^[2]. The great difference is derived from the change of R-2 molecule structure. The precursor exhibits stronger CD signals with positive and negative Cotton effect in its circular dichroism spectrum (Fig.3). The molecular ellipticity of precursor is: $[\theta]_{\lambda}=+1.51\times10^5$ (253.0 nm), -1.99×10^5 (271.6 nm), $+1.53\times10^4$ (312.6 nm); and the molecular ellipticity of R-1 is: $[\theta]_{\lambda}=-1.50\times10^5$ (244.4 nm), $+8.58\times10^3$ (287.8 nm), $+5.11\times10^3$ (329.6 nm). The largest ellipticity of R-1 with Cotton effect was observed at 244 nm, the R-1 ellipticity $[\theta]_{\lambda}$ of Cotton effect was weaker, the long wavelength CD effect of R-2 is regarded as the effectively extended conjugated structure. Cotton effect of the CD spectra of R-1 and R-2 is consistent with their UV absorption position and intensity^[10,16].

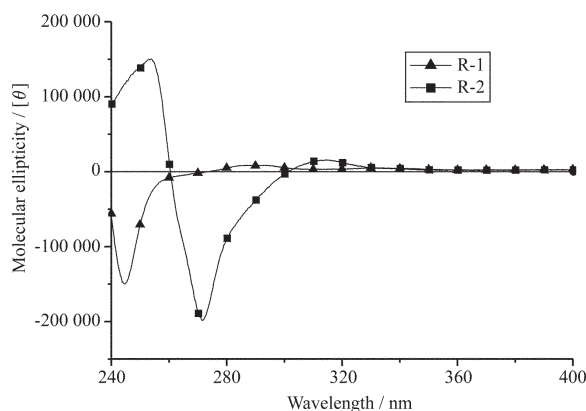


Fig.3 CD spectra of R-1 and R-2

The Heck coupling reaction was found to offer a very simple access to the silylated precursor incorpo-

rated optically active BINOL moities. The precursor was hydrolyzed by the sol-gel process to give the corresponding silica hybrid xerogel under the mild condition. Both precursor and xerogel incorporating the functional chiral BINOL moities could open new perspectives in the development of solid supports for heterogeneous asymmetric catalyst and chiral molecular recognition. Furthermore, xerogel material shows interesting tunable property which makes them potential candidates for the development of enantioselective fluorescent chemosensors for the separation of chiral molecules.

References:

- [1] Moreau J J E, Michel W C M. *Coord. Chem. Rev.*, **1998**, **178**:1073~1084
- [2] Anne B, Hesemann P, Luc R, et al. *J. Organometallic Chem.*, **2001**, **627**:239~248
- [3] Dubois G, Catherine R, Corriu R J P. *J. Mater. Chem.*, **2000**, **10**:1091~1098
- [4] Hesemann P, Moreau J J E. *Tetrahedron: Asymmetry.*, **2000**, **11**:2183~2194.
- [5] Chevalier P, Corriu R J P, Moreau J J E. *New J. Chem.*, **1998**, 423~433
- [6] Adima A, Moreau J. J E, Michel W C M. *J. Mater. Chem.*, **1997**, **7**:2331~2333
- [7] Broudic J C, Conocar O, Moreau J J E. *J. Mater. Chem.*, **1999**, **9**:2283~2285
- [8] Zhang X Z, Bradshaw J S, Izatt R M. *Chem. Rev.*, **1997**, **97**:3313~3362
- [9] Pugh V J, Hu Q S, Pu L. *Angew. Chem., Int. Ed.*, **2000**, **39**:3638~3640
- [10] Pu L. *Chem. Rev.*, **1998**, **98**:2405~2494
- [11] Hu Q S, Dilrukshi V, Pu L. *Tetrahedron: Asymmetry.*, **1995**, **6**:2123~2126
- [12] Koichi T, Toru O, Fumio T. *Angew. Chem., Int. Ed.*, **1993**, **32**:1147~1151
- [13] Brisdon B J, England R, Reza K, et al. *Tetrahedron*, **1993**, **49**:1103~1114
- [14] Armin M, Frnk E M. *Angew. Chem., Int. Ed.*, **1994**, **33**:2379~2411
- [15] CHENG Yi-Xiang (成义祥), LIU Tian-Dong (刘田东), CHEN Ling-Wu (陈令武). *Zhongguo Huaxue (Chin. J. Chem.)*, **2003**, **21**:1101~1104
- [16] Hua C, Ma L, Pu L. *Tetrahedron: Asymmetry.*, **1996**, **7**:3083~3086